CONTRACT NO: A832-126
FINAL REPORT
OCTOBER 1991

Development of a Universally Accepted Test Method for Volatile Organic Compounds

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

DEVELOPMENT OF A UNIVERSALLY ACCEPTED TEST METHOD FOR VOLATILE ORGANIC COMPOUNDS

Final Report
Contract No. A832-126

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DEVELOPMENT OF A UNIVERSALLY ACCEPTED TEST METHOD

FOR

VOLATILE ORGANIC COMPOUNDS

ACKNOWLEDGEMENTS

This report was submitted in fulfillment of Contract #A832-126, Development of a Universally Accepted Test for Volatile Organic Compounds by Calcoast Analytical-ITL Labs under sponsorship of the California Air Resources Board. Laboratory work was completed as of January 1991. We wish to acknowledge the aid of Dr. R. Grant of the Air Resources Board for his constructive comments and Mr. F. Vegara also of the Air Resources Board for his help in the coating sample collection.

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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ABSTRACT

Test methods published by the American Society for Testing and Materials (ASTM) and used for the determination of Volatile Organic Compound (VOC) content of coatings are known to have cumulatively poor reproducibility. The VOC calculations are contained in ASTM D3960 which comprises methods D1475 for density D2369 for percent weight of non-volatiles; D3792 and D4017 for water content, and D4457 for chlorinated hydrocarbon content.

Test methodology, adequacy or appropriateness of instrumentation and competence of laboratory personnel are variables addressed in this work.

Some of the problems associated with compositionally unusual and unique coating systems with respect to the determination of non-volatile content and water content are discussed.

Proposed revisions to the test protocols are given which greatly improve interlaboratory reproducibility.

The work shows that good reproducibility in VOC determinations for coatings are a function of procedural improvements, level of operator competence and quality of instrumentation.

1. INTRODUCTION

Industrial and architectural coatings produce a significant amount of air pollution in California through the emission of Volatile Organic Compounds (VOC) inherent to those coatings. Thus, there is an absolute necessity to accurately measure the Volatile Organic Compound (VOC) Content of those coatings so their contribution to atmospheric pollution in California can be monitored and kept to a minimum.

Currently, the available test methods used for measuring the Volatile Organic Compound (VOC) Content of waterborne and solvent-based coatings introduced from new technology have high reproducibility errors. These high reproducibility errors make the enforcement of current VOC limits by local Air Quality Management Districts very difficult. Poor reproducibility in the test methods allows the coating manufacturer to exceed a specified VOC content limit by more than ten percent. The components of the final VOC calculation using the current ASTM testing protocol allows such large reproducibility variations that the final reproducibility greatly exceeds 10%.

ASTM Method and Reproducibility

Method Number	Method	Reproducibility
D 1475 - 60	Density	1.5%
D 3792	Water (GC)	7.5%
D 4017 - 81	Water (KF)	15.0%
D 2369 - 81	Non-volatile	7.1% 20 min
		4.7% 60 min
D 4457 - 85	Exempt	8.1% TCA
	Solvent	17.9% DCM

Calcoast has modified the existing test methods for measuring the VOC content of new technology waterborne and solvent-based coatings, in an attempt to increase the accuracy, precision, and reproducibility of the VOC content measured.

The development of a universally accepted test method for measurement of VOC emissions will allow much more stringent enforcement by regulatory agencies. This enforcement will ultimately produce a considerable reduction in the contribution from coatings to air pollution in California.

2. SAMPLING PROCEDURE AND COLLECTION

A. Coating samples collected by the California Air Resources Board (CARB)

A total of eighty-three (83) solvent-based and waterborne coating samples were collected by Mr. F. Vegara of the California Air Resources Board. The two(2) California Air Quality Districts which participated in the sample collection were the South Coast Air Quality Management District (SCAQMD) and the San Diego Air Quality Management District (SDAQMD). The coating samples collected by the California Air Resources Board included single and multiple component waterborne and solvent-based systems. Complete mixing ratios were provided for all multiple component samples. Any VOC content information known or provided by the coating manufacturer was intentionally omitted. All samples collected were given an Air Resources Board (ARB) number. A complete description of all coating samples collected was provided and is included with this report under Section 20, Appendix D.

B. Coating samples provided by the laboratory

Calcoast Labs provided twenty-five (25) coating samples. The samples included both single and multiple component waterborne and solvent-based systems. The samples used for the improvement and evaluation of VOC measurement methods were either provided to the laboratory by the coating manufacturer or formulated in-house specifically for the VOC study. Problem coatings such as those containing high water/low solids and high solvent/low solids were intentionally included in the VOC study.

3. PROPOSED Method for Water Content by Gas Chromatography -- Summary and Discussion of Results

A. Types of Waterborne Coatings Analyzed

The water content using the proposed modifications to ASTM D3792 was measured for a total of eight (8) types of waterborne coatings. The coatings analyzed included:

1. Emulsions
2. Solution Resins
3. Primers/Sealers
4. Terpolymers
5. Baking Alkyds
6. Urethanes
7. Urethane/Acrylics
8. Alkylalkoxysilanes(silanes)

B. Reasons For the Proposed Modifications to ASTM D3792

The injector temperature was increased due to possible condensation problems occurring at the injector port leading to an over-response of the thermal conductivity (TC) detector to water. The higher column temperature yields a sharper end-point (reference peak). An extremely important criteria is the reference side of the thermal conductivity bridge must have the identical flow rate of carrier gas and identical column as that used for the sample side of the bridge. This ensures maximum response and sensitivity of the detector for the compounds being analyzed. The same column conditioning procedure must be used for the reference column. A final column temperature hold at 210^0C for twelve (12) minutes allows maximum column/detector clean-up between subsequent runs. The increased diluent, sample, and internal standard size allows a more representative aliquot of the coating sample and increased separation of resin solids/pigment from supernatant. One drawback to this approach is that if contaminants (H_2O) are present in the diluent and/or internal standard these levels also will be increased. They can, however be corrected for in the water content calculation by analyzing the diluent and internal standard individually for water content. While DMF is compatible with most waterborne systems, some coatings such as solution resins may present compatibility problems. Butyl cellosolve can be used as an appropriate diluent under such circumstances.

C. Proposed Modifications to ASTM D3792 -- Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph

Parameter	ASTM D3792	Modification
a. Detector Temperature	240°C	240°C
b. Injection Temperature	200°C	240°C
c. Carrier Gas flow rate mls/min	50	36 helium recommended
d. Column		
1. Type	PORAPAC Q	PORAPAC Q
2. Length	4 ft	8 ft
3. Mesh	60/80	80/100
e. Column Temperature°C		
1. Initial	80	75
2. Final	170	210 12 min. hold
3. Program Rate	30C/min	12C/min.
f. Liquid charging Device	10 or 25 ul syringe	5 ul
g. Sample Preparation		
1. Size	0.6g	1.2g
2. Internal Standard	0.2g	0.5g
3. Diluent (DMF) amount	2 mls	6 mls

D. Discussion of Results

1. Emulsions

When using isopropyl alcohol (IPA) as the internal standard and dimethylformamide (DMF) as the diluent, the percent recovery obtained was 105. This was based on emulsion systems containing approximately forty (40) percent (w/w) water and spiking the coating sample with forty (40) percent (w/w) water. Duplicate samples were analyzed and produced numbers of 43.61 and 43.41 percent water (w/w), yielding a Relative Percent Difference (RPD) of 0.46. Modifications to ASTM D3792 used to achieve these results are described in Part B.

2. Solution Resins

When using DMF as the diluent, an erroneously high water content resulted (approximately seven percent). When the diluent was changed to butyl cellosolve the results obtained were much better. Water content was within 0.3 percent (w/w) of the manufacturer's claim, percent recovery was 111, and RPD between duplicates was 0.89. Modifications to ASTM D3792 used to achieve these results are described in Part B.

D. Discussion of Results-Continued

3. Primers/Sealers

The primer/sealer analyzed had a density of 10.82 lbs/gal (1.29 g/ml). The total solids was 44.48 percent (w/w). IPA was used as the internal standard and DMF as the diluent[1]. Duplicate samples were prepared/analyzed separately. The coating sample was spiked with water at ten (10), forty (40), and seventy (70) percent (w/w) levels. Percent recovery, RPD, and water content are given in **TABLE 1. Summary of Water Content of Coatings Using Proposed Test Method for Water Content by GC - ASTM D3792.**

4. Terpolymers

The terpolymer coating had a density of 10.90 lbs/gal (1.31 g/ml). The total solids level was 61.87 percent (w/w). IPA was used as the internal standard and DMF as the diluent[1]. Duplicate samples were prepared/analyzed separately. The coating sample was spiked with water at ten (10), forty (40), and seventy (70) percent (w/w) levels. Percent recovery, RPD, and water content are given in **TABLE 1. Summary of Water Content of Coatings Using Proposed Test Method for Water Content by GC - ASTM D3792.**

5. Baking Alkyds

The baking alkyd had a density of 9.36 lbs/gal (1.12 g/ml). The total solids level was 61.77 percent (w/w). IPA was used as the internal standard. The proposed diluent was DMF, but incompatibility problems existed (a cloudy separation of pigment/resin solids from supernatant resulted).

D. Discussion of Results -- Continued

5. Baking Alkyds

The diluent chosen was butyl cellosolve which was much more compatible with the system and yielded a clear supernatant after centrifugation. Duplicate samples yielded an average water content of 35.76 percent (w/w) with an RPD of 0.23. The VOC of the coating was determined to be 45.9 g/L while manufacturer claimed it to be approximately 60.0 g/L.

6. Urethanes

DMF was chosen as the diluent which yielded a clear supernatant and presented no other compatibility problems. IPA again was used as the internal standard. Duplicate samples yielded an average water content of 53.68 percent (w/w) with a RPD of 0.39.

7. Urethane/Acrylics

DMF was chosen as the diluent which presented no compatibility problems. The internal standard was IPA. Duplicate samples yielded an average water content of 52.49 % w/w with a RPD of 0.51 between duplicates.

8. Alkylalkoxysilane (silanes)

The silane system had a density of 8.09 lbs/gal (0.97 g/ml). The total solids level was 9.50 % w/w. IPA was used as the internal standard. DMF was used as the diluent which presented no compatibility problems. Duplicate samples yielded an average water content of 84.78 % w/w with a RPD of 0.32 between duplicates. The measured VOC of the coating was 311 g/L while the manufacturer claimed it be less than 350 g/l.

Table 1. Water Content by GC Using Proposed Modifications to ASTM D3792

Coating Type	Water Content %(w/w)	RPD	Diluent	Percent Recovery	Comments
a. Emulsions	43.51	0.46	Dimethyl-Formamide (DMF)	105 at 40 percent (w/w) spike level	-
b. Solution Resins	38.60	0.89	Butyl Cellosolve	111 at 40 percent (w/w) spike level	Coating system was incompatible with diluent (DMF) leading to an erroneously high water content (7 percent).
c. Primer/Sealer Emulsions	50.39	0.38	DMF	at 10 percent spike level 100 at 40 percent spike level - 98 at 70 percent spike level - 96	Coating had a density of 10.90 lbs/gal Total solids were 44.48 % (w/w).
d. Terpolymer Emulsion	35.77	0.12	DMF	at 10 percent spike level - 100 at 40 percent spike level - 97 at 70 percent spike level - 95	Coating had a a density of 10.90 lbs/gal Total solids were 61.87 % (w/w).

TABLE 1 - CONTINUED

Coating Type		Water Content % (w/w)	RPD	Diluent	Percent Recovery	Comments
e.	Waterborne Baking	35.75	0.23	Butyl cellosolve	-	Coating system was incompatible with DFM. Coating density was 9.36 lbs/gal Total solids were 61.77 % (w/w).
f.	Urethane	53.68	0.39	Dimethyl-formamide	- -	- -
g.	Urethane/ Acrylic emulsion	52.49	0.51	Dimethyl-formamide	-	-
h.	Alkylalkoxy-silane (silane)	84.78	0.32	Dimethyl-formamide	-	The coating density was 8.09 lbs/gal Total solids were 9.50 % (w/w).

Total coatings analyzed: 24

4. PROPOSED vs. EXISTING GC WATER -- Comparison of Proposed versus Existing Test Method for Water Content of Water-reducible Paints by Direct Injection into a Gas Chromatograph (ASTM D3792)

A. Discussion of Results

1. Modified Test Procedure

The reproducibility (relative %) numbers obtained for both modified and unmodified versions of ASTM D3792 reflect an average of eight (8) separate analyses performed. This includes coating samples with low, medium, and high water content. Different operators on different days using the modified ASTM D3792 specification obtained reproducibility (relative %) numbers for coatings with low, medium, and high water content of **0.3, 0.7,** and **1.0**, respectively. These numbers are given in **TABLE 2. Water Content by GC - ASTM D3792** and also in **FIGURES** 1 and 2.

2. Existing (Unmodified) Test Procedure

Different operators on different day using the unmodified (original) ASTM D3792 specification obtained reproducibility (relative %) numbers for the coatings with low, medium, and high water content of **10.5, 4.6,** and **6.0**, respectively. These numbers are given in **TABLE 2. Water Content by GC - ASTM D3792** and also in **FIGURES** 1 and 2. While the coatings samples with low water had a relative reproducibility of 10.5, the coating samples with medium and high water are in agreement with the QC/QA criteria of relative reproducibility of **7.5%** as stated in the original ASTM D3792 specification.

Table 2. Water Content by GC Using Proposed Modifications to ASTM D3792 as a Function of Day and Operator

Coating	DAY 1 OP1	DAY 1 OP2	DAY 2 OP1	DAY 2 OP2	Theo-retical	RPD	Repro-ducibility* (Relative %)[5]
	Water Content[2] (w/w)						
A. Modified[3]							
1. Terpolymer Emulsion (low water)	35.77	35.89	35.67	35.35	35.00	0.12	0.3
2. Acrylic Emulsion (mid water)	40.30	44.89	45.41	45.10	45.90	0.20	0.7
3. Silane (high water)	84.78	84.66	84.67	84.89	85.00	0.32	0.1
B. Unmodified[4]							
4. Terpolymer Emulsion (low water)	20.35	24.41	21.76	13.49	35.00	32.2	10.50
5. Acrylic Emulsion (mid water)	22.89	17.71	20.45	27.69	45.90	40.0	4.6
6. Silane (high water)	80.18	75.93	80.38	75.27	85.00	0.87	6.0

* Between Operators

[2] Water Content results given are an average of duplicates obtained by each operator on a given day.

[3] Modifications in ASTM D3792 - "Water Content of Water Reducible paints by Direct Injection into a Gas Chromatograph", used to achieve these results are given in section 3D.

[4] Unmodified refers to using the original ASTM D3792-86 Specification as printed.

[5] Reproducibility between operators (Relative %) results are calculated as an average between two (2) results obtained by two (2) different operators on two (2) different days (see Figures 1, 2, and 3).

Figure 1. Comparison of absolute error using modified and unmodified ASTM D3792

FIGURE 1

INTRALABORATORY ABSOLUTE ERROR/THEORETICAL VALUE

USING MODIFIED AND UNMODIFIED ASTM D3792

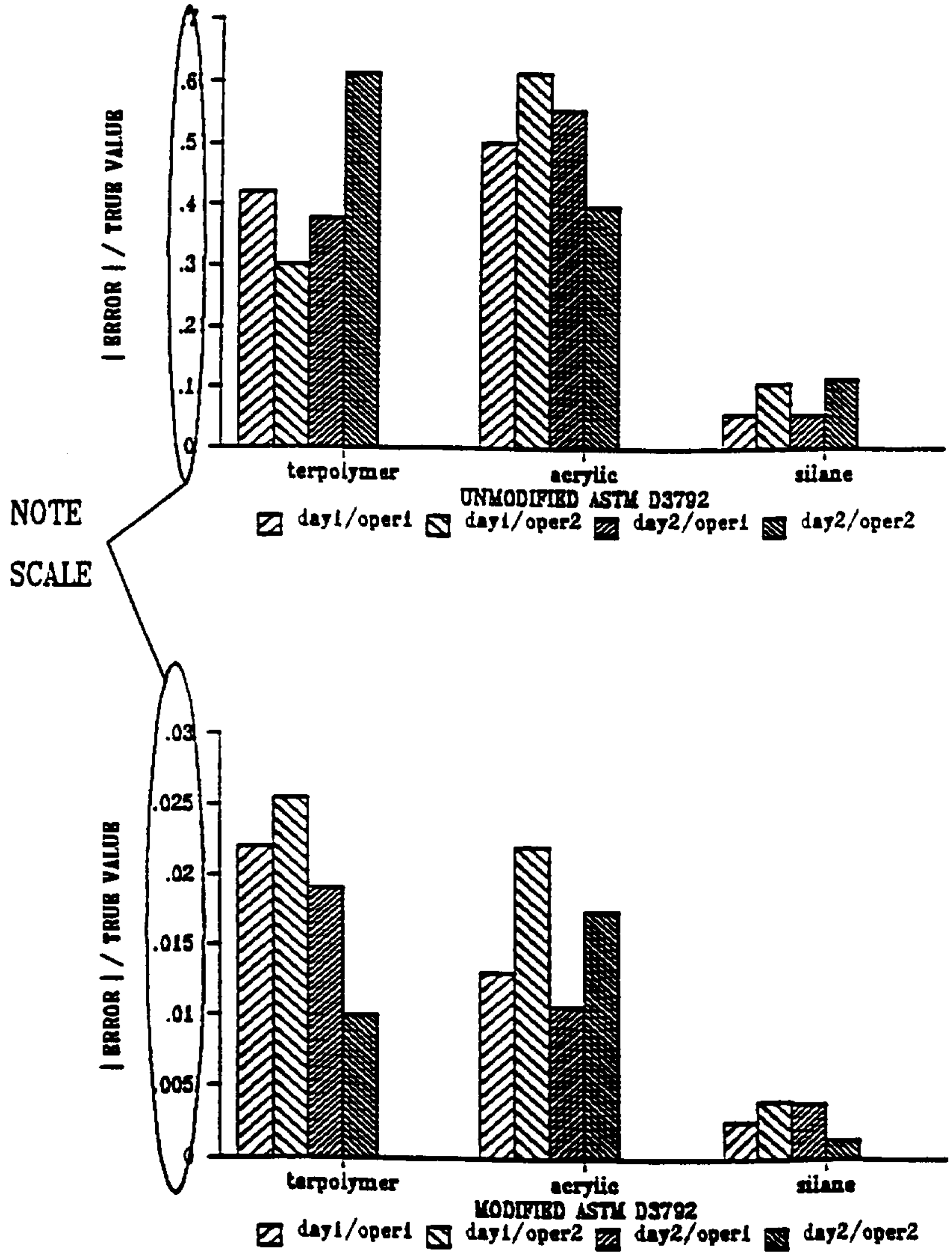
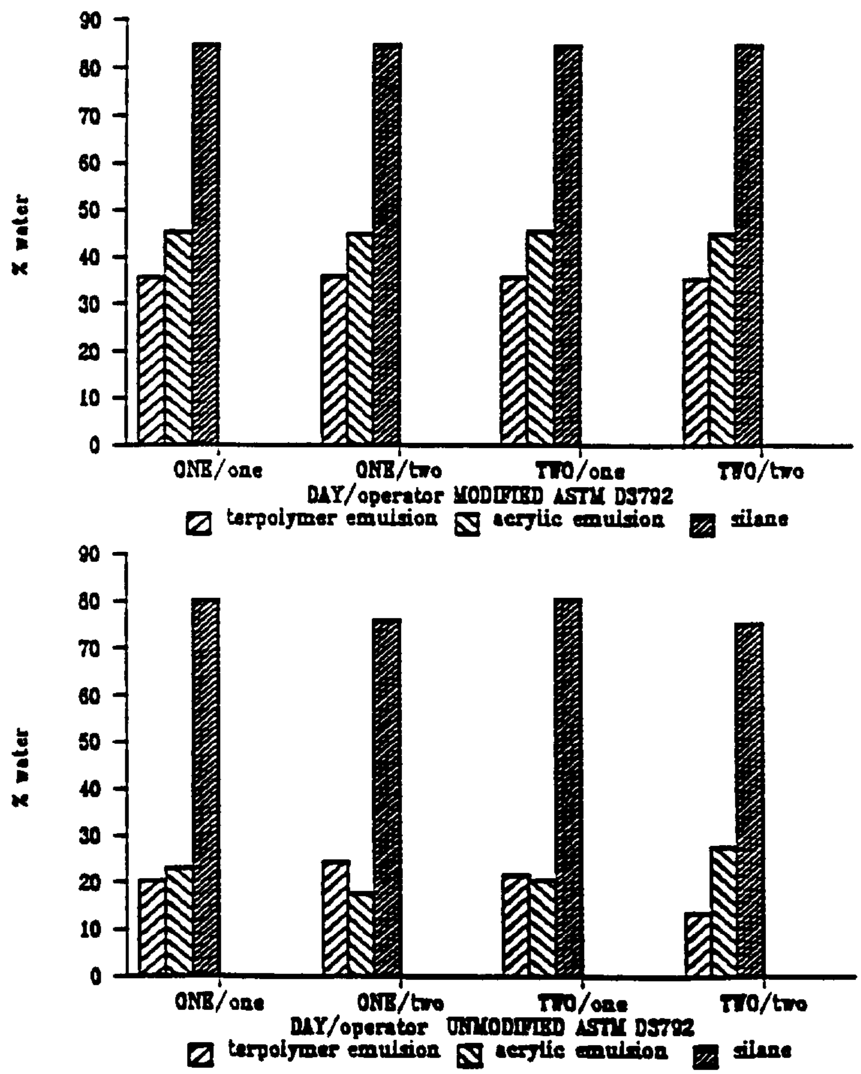


Figure 2. Intralaboratory comparison between days and operators using modified and unmodified ASTM D3792

FIGURE 2

INTRALABORATORY COMPARISON BETWEEN OPERATORS

USING MODIFIED AND UNMODIFIED ASTM D3792



5. EXPERIMENTAL KF WATER -- Experimental Test Methods for Water in Paints and Paint Materials by Karl Fischer Titration (ASTM D4017)

A. Discussion of Method

Calcoast Labs conducted an intralaboratory survey for water content of waterborne coatings using Karl Fischer (KF) titration. The coating samples were analyzed with and without the 1-ethylpiperidine catalyst using both manual and automatic titrators. Whether the titrator was automatically or manually operated did affect the precision, accuracy, and reproducibility of the water content determination. The intralaboratory survey included using different operators on different days analyzing the same samples using the same instrumentation. The coating samples analyzed contained low, medium, and high concentrations of water. Types of coating samples analyzed consisted of emulsions, electrostatic primers, ter-polymer emulsions and silane systems.

B. Discussion of Results

Different operators on different days using no 1-ethylpiperidine catalyst and an automatic KF Titrator obtained Reproducibility (relative %) numbers ranging between **1.7** and **0.4** for coating samples with low, medium, and high concentrations of water. The ter-polymer emulsions (low water) analysis produced the highest reproducibility (relative %) number and was **1.7**. The silane (high water) analysis produced the lowest reproducibility number and was **0.4** (relative %). Overall, the reproducibility numbers were lower (between 1-5%) than those using the manual KF titrator. These numbers are given below in bold type in **TABLE 4.** All reproducibility numbers obtained are below the QC/QA criteria of **15.0** as stated in the original ASTM D4017 specification.

Table 3. Water Content by Karl Fischer Using a Manual Titrator, No Catalyst

Coating	DAY 1 OP1	DAY 1 OP2	DAY 2 OP1	DAY 2 OP2	THEO-* RETICAL	RPD	S	RPR
1. Emulsion (low water)	42.31	42.08	40.33	43.91	45.03	4.1	2.2	2.0
2. Emulsion (mid water)	61.27	61.02	59.61	58.32	60.15	1.3	2.5	0.6
3. Electrostatic primer (high water)	69.48	70.34	76.87	70.13	71.80	2.1	6.0	1.1
4. Emulsion (high water)	75.74	75.29	69.81	74.96	73.45	3.0	4.8	1.5
5. Emulsion (high water)	78.33	78.69	74.89	77.89	77.60	8.9	3.1	4.5
6. Ter-polymer emulsion (low water)	20.05	23.35	20.74	23.45	35.00	13.7	3.5	6.9
7. Silane (high water)	72.53	75.13	72.79	75.29	75.00	3.4	2.9	1.7

*Theoretical water content provided by manufacturer
RPR - relative percent reproducibility
RPD - relative percent difference
S - standard deviation

Equations Used:

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} X 100$$

Where: D1 = First sample value.
D2 = Second sample value (duplicate).

$$s = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n - 1}}$$

where:
s = estimated standard deviation of the series of results,
X_i = each individual value,
$\bar{X}$ = average (arithmetic mean) of all values, and
n = number of values.

(RPR) = Coefficient of Variation X Factor at 95 Percent Confidence Level for x degrees of freedom

Coefficient of Variation = $\frac{(s_i \times 100)}{\bar{X}}$

No. of Samples = 8 for each category

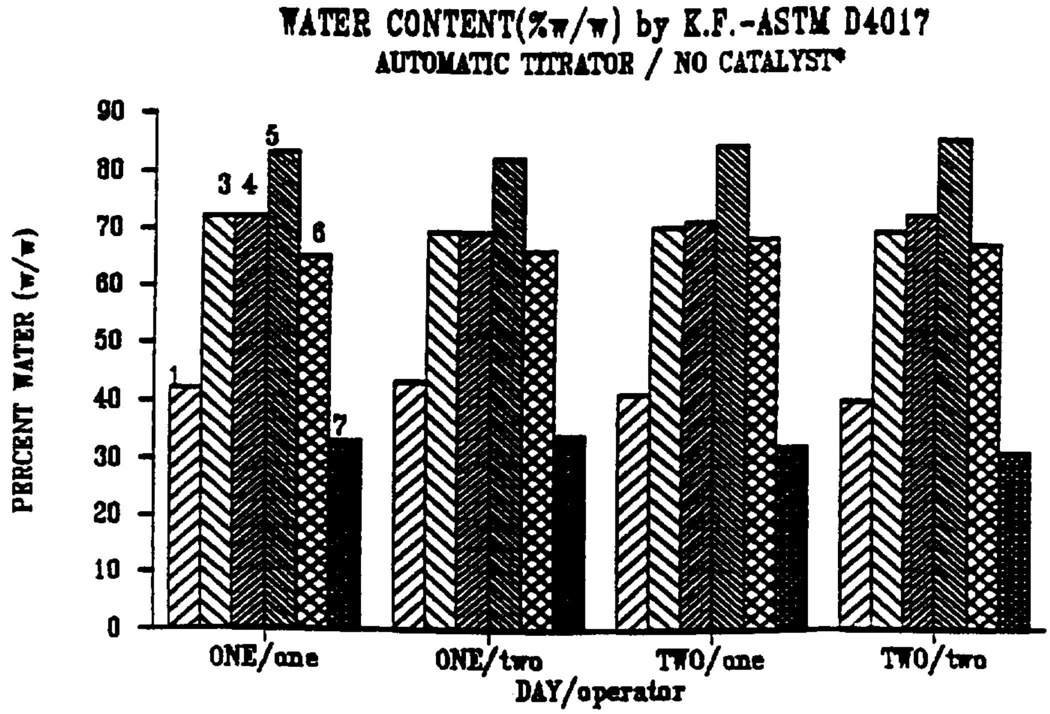
Table 4. Water Content by Karl Fischer Using an Automatic Titrator, No Catalyst

Coating	DAY 1 OP1	DAY 1 OP2	DAY 2 OP1	DAY 2 OP2	THEO-* RETICAL	RPD	RPR**
1. Emulsion (low water)	44.11	45.03	42.28	43.15	45.03	2.1	1.1
2. Emulsion (mid water)	51.11	59.63	59.41	58.32	60.15	3.1	1.6
3. Electrostatic primer (high water)	72.72	69.20	66.20	72.03	71.80	1.6	0.8
4. Emulsion (high water)	81.28	76.31	75.88	78.21	73.45	1.7	0.9
5. Emulsion (high water)	67.34	70.28	70.05	70.96	77.80	2.8	1.4
6. Ter-polymer emulsion (low water)	32.16	32.05	34.18	32.15	35.00	3.3	1.7
7. Silane (high water)	76.17	75.35	75.25	74.89	75.00	0.8	0.4

*Theoretical water content provided by manufacturer
**RPR - relative percent reproducibility
RPD - relative percent difference

Figure 3. Water content by Karl Fischer Titration ASTM D4017

FIGURE 3



1) EMULSION (low water)

3) ELECTROSTATIC PRIMER (high water)

4) EMULSION (low water)

5) EMULSION (high water)

6) TERPOLYMER EMULSION (low water)

7) SILANE (high water)

* PRESCRIBED CATALYST IN ASTM D4017 IS 1-ETHYLPIPERIDINE

B. Water Content by KF Titration using a catalyst of 1-ethylpiperidine

1. With a Manual KF Titrator

Both the acetone and methyl ethyl ketone (MEK) solvents affected the accuracy of the water content by KF titration. Using the manual KF titrator the acetone spike (11.7% w/w) produced a low water content with and without the 1-ethylpiperidine catalyst. The theoretical water content was 45.06 and water content measured ranged between 34 and 35 percent. The methyl ethyl ketone (MEK) spike (10.2% w/w) produced results similar to those obtained with acetone spike using the manual KF titrator with and without the catalyst.

2. With an Automatic KF Titrator

The water content determination using the automatic KF titrator produced results similar to those using the manual titrator except the accuracy was better with and without the 1-ethylpiperidine catalyst. Water content measured ranged between 39-41 percent. These numbers are given below in Table 5.

Table 5. Water Content (% w/w) by Karl Fischer Titration, With Interfering Solvents

A. Manual KF Titrator-Not Microprocessor Controlled

COATING	1-EP[3]	NO-EP[5]	THEO-RETICAL	SPIKING COMPOUND[4]	SPIKE LEVEL (% W/W)
1. Emulsion (low water)	33.94	35.04	45.06	acetone	11.7
2. Emulsion (high water)	77.46	69.22	--	methyl ethyl ketone (MEK)	10.2

B. Automatic KF Titrator-Not Microprocessor Controlled

COATING	1-EP[3]	NO-EP[5]	THEO-RETICAL	SPIKING COMPOUND	SPIKE LEVEL (% W/W)
1. Emulsion (low water)	40.84	38.56	45.06	acetone	11.7
2. Emulsion (high water)	68.60	70.14	--	methyl ethyl ketone (MEK)	10.2

[3] 1-EP-using 1-ethylpiperidine catalyst
[4] Both spiking compounds contained <0.01% H_2O
[5] No-EP-no ethylpiperidine catalyst used

Figure 4. Comparison of results between days and operators using ASTM D4017

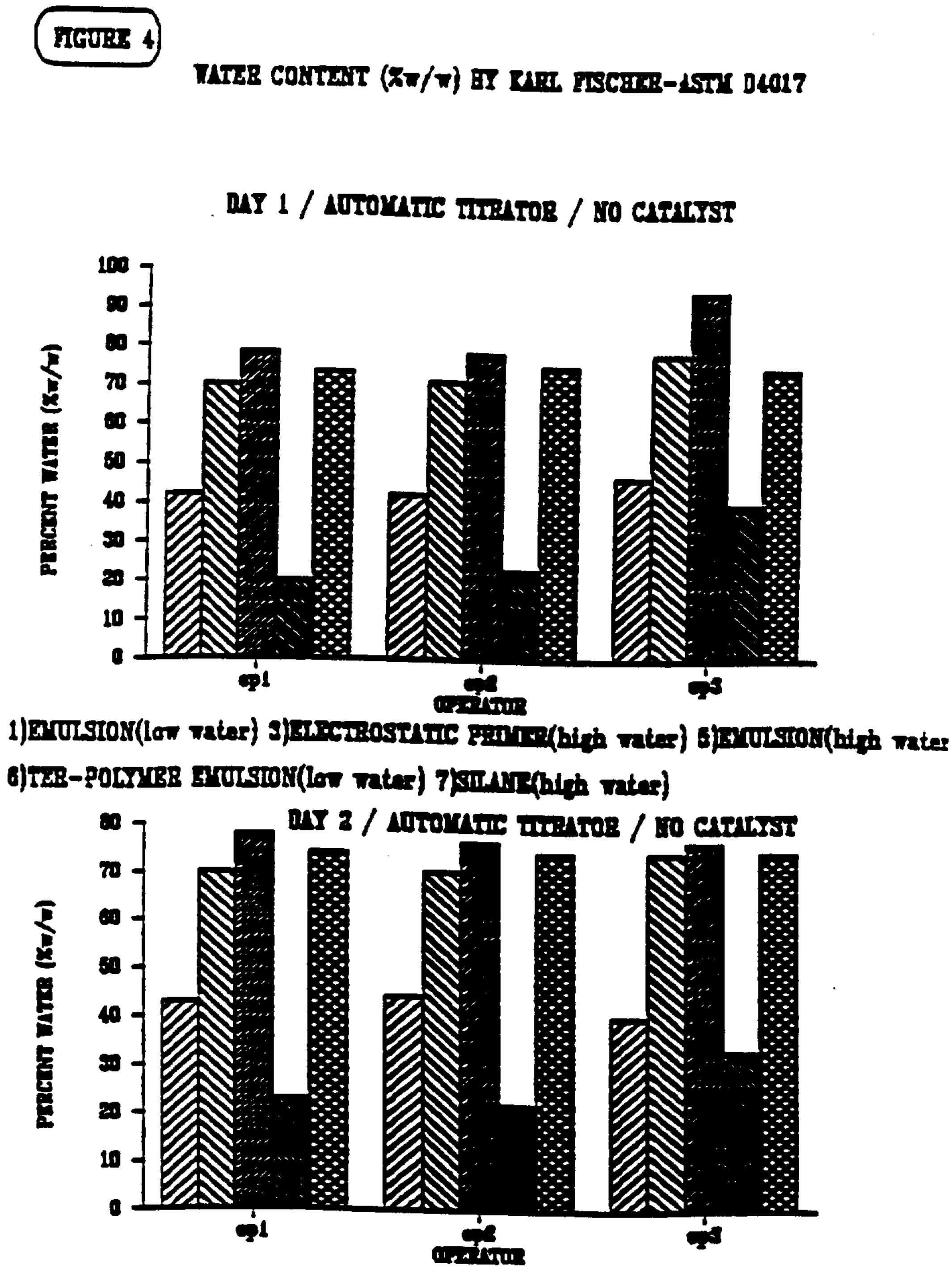


Table 6. Water Content by ASTM D4017

Summary of water content of waterborne coatings systems analyzed by Karl Fischer titration - ASTM D4017

Coating Type	1-Ethylpiperidine used	Comments
1. emulsion (low water)	no	Coating did not disperse well. Electrode response sluggish and endpoint detection difficult.
	yes	Electrode response much sharper but needle still fluctuates at endpoint.
2. Emulsion (high water)	no	Coating dispersed well, endpoint very sharp.
3. Electrostatic primer (high water)	no	Coating dispersed well, endpoint sharp.
	yes	Coating dispersed well, endpoint sharp.
4. Emulsion (high water)	no	Coating did not disperse well. Electrode response sluggish and end-point detection difficult.
	yes	Coating dispersed much better. End-point was very sharp.

TABLE 6 - continued

Coating Type	1-Ethylpiperidine used	Comments
5. Emulsion (high water)	no	Coating partially dispersed. Electrode response somewhat sluggish.
	yes	Coating dispersed well. Endpoint very sharp.
6. Ter-Polymer (low water)	no	Coating sample dispersed extremely poor. Electrode response was irratic. Endpoint detection was very difficult.
	yes	Coating sample dispersed somewhat. Endpoint more stable, but still electrode response still fluctuated.
7. Silane (high water)	no	Coating dispersed well. Endpoint was sharp.
	yes	Coating dispersed readily. Endpoint was very sharp.

C. Use of a Micro-processor Controlled Karl Fischer Titrator for Water Content Determination for Coatings.

1. Instrument features

   a. Single Burette titration System rapid measurements with accuracy ± 0.15%, 0.01% reproducibility.

   b. Background correction improves accuracy by automatically correcting for atmospheric moisture contamination.

   c. Detector - provides visual status of titration

      Green - Titration is in progress
      Yellow - End point near
      Red - Titration complete

   d. Time delayed titrations - titration can automatically begin after pre-set time for sample dissolution.

   e. Air tight titration cell increases accuracy by eliminating
      ambient moisture contamination.

   f. Printer provides complete documentation of analysis and graphical display of titration.

   g. Detection sensitivity 0.1 g H_2O.

2. Waterborne coating sample analysis

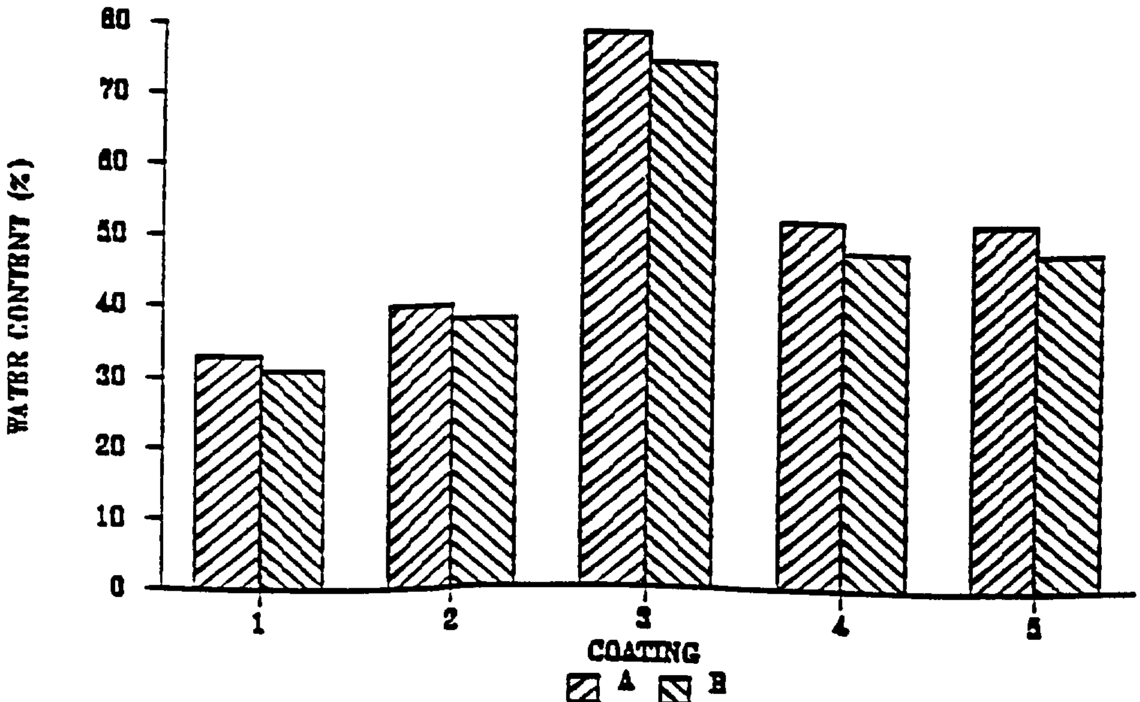
   Five (5) waterborne coating samples were analyzed in quadruplicate using one hundred (100) percent methanol as diluent. The coatings analyzed included a silane system, a mid-acrylic emulsion, a electrostatic primer, and two (2) low solids vinyl/acrylic emulsions. The Relative Percent Difference (RPD) varied somewhat ranging from 0.08 for the silane system to 2.51 for the vinyl/acrylic emulsion. The time to endpoint between sample types varied between 3 and 23 minutes. These water content numbers obtained are displayed graphically in Figure 11.

   Five (5) additional waterborne coatings were analyzed in triplicate using five (5) combinations of solvents. The coatings analyzed included a high-build water-based ter-polymer coating, a fire retardant acrylic roofing material, a water-based wood sealer, and two (2) latex samples. The solvents used included 100 % pyridine, 50 % methanol/50 % formamide, 100 % methanol, and 50 % methanol/50% Dimethyl-formamide (DMF). The same five (5) coatings were also spiked with an interfering solvent (methyl ethyl ketone).

Figure 5. Water content determination by Karl Fischer Titration using 100% methanol as solvent

FIGURE 5

The Effect of an Interfering Solvent (MEK) on the Water Conte Determination using a Microprocessor Controlled K.F. Titrator 100% Methanol as Solvent



A) ORIGINAL (theoretical) WATER CONTENT

B) WATER CONTENT with MEK Interferent

1) High-Build Waterborne Terpolymer Coating

2) Fire Retardant Acrylic Roofing Material

C) Waterborne Wood Sealer

D) Latex Based Coating

E) Latex Based Coating

3. Discussion:

Using one hundred (100) percent methanol for the water content determination appears to be as effective as the more toxic pyridine, formamide, and dimethyformamide solvents. The Relative Percent Difference (RPD)using methanol ranged for 0.19 to 0.64. The Relative Percent Difference using 50% methanol/50% DMF ranged from 0.06 to 0.61. The Relative percent Difference using 100 percent pyridine ranged from 0.44 to 2.05. The Relative Percent Difference using 50% Methanol/50% formamide ranged 0.08 to 2.06. These numbers are given in **TABLES 7, 8, 9, 10,** and **11** and displayed graphically in Figures 6, 7, 8, 9, and 10.

When using methanol as the solvent, the presence of interfering solvents such as methyl ethyl ketone (MEK) slightly effect the water content determination. The Relative Percent Difference (RPD) ranged from 0.01 to 1.42 when compared to the water content of the samples without the MEK solvent present. These numbers are given in **TABLE 12** and displayed graphically in Figure 10.

4. Example of a water based coating analysis

DATE	4/26/90
SAMPLE NO	1
FACTOR	5.925 mg
TITER	18.59 ml
BLANK	0.000 ml
H_2O	110.15 mg
SIZE	0.9859 g
	- 0.6608 g
	0.3251 g
H_2O	33.88

1 MIN	27.67 %
2 MIN	31.47 %
3 MIN	32.53 %
4 MIN	32.84 %
5 MIN	33.06 %
6 MIN	33.06 %
7 MIN	33.39 %
8 MIN	33.52 %
9 MIN	33.61 %
10 MIN	33.68 %
11 MIN	33.75 %
12 MIN	33.81 %
13 MIN	33.84 %
14 MIN	33.88 %

Table 7. Water Content of a Terpolymer

The Effect of Different Diluents on the Water Content Determination of a High-build Waterborne Terpolymer Coating.

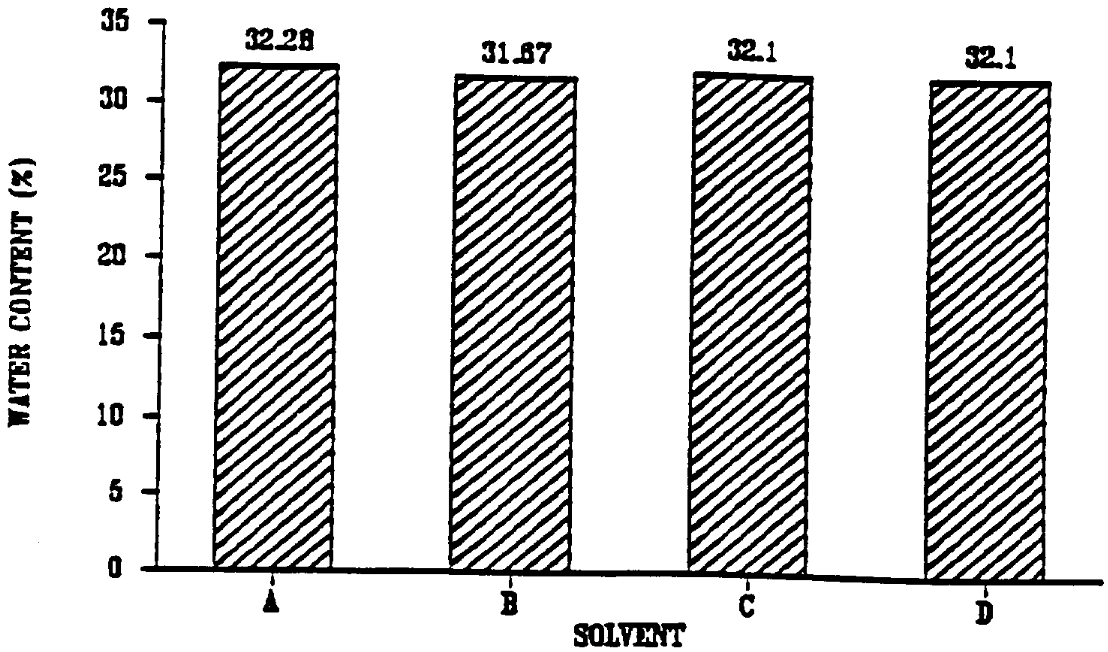
Type of diluent	RPD[1]	Water Content % (w/w) Average	Time to Endpoint (minutes)
a. 100% pyridine	0.75	32.28	3
b. 50% v/v methanol 50% v/v formamide	1.17	31.67	6
c. 100% methanol	0.19	32.10	6
d. 50% v/v methanol 50% v/v DMF	0.19	32.10	10

[1] RPD = Relative Percent Difference from Theoretical Value

Figure 6. Water content of a terpolymer using ASTM D4017 with various solvent systems

FIGURE 6

WATER CONTENT of a High-Build Waterborne Terpolymer Coating by K.F. Titration using Varying Solvents



A) 100% PYRIDINE

B) 50% METHANOL / 50% FORMAMIDE (v/v)

C) 100% METHANOL

D) 50% METHANOL / 50% DMF (v/v)

Table 8. Water Content of an Acrylic Roofing Material Using Various Solvent Systems

The Effect of Different Diluents on the Water Content Determination of a Fire retardant Acrylic Roofing Material

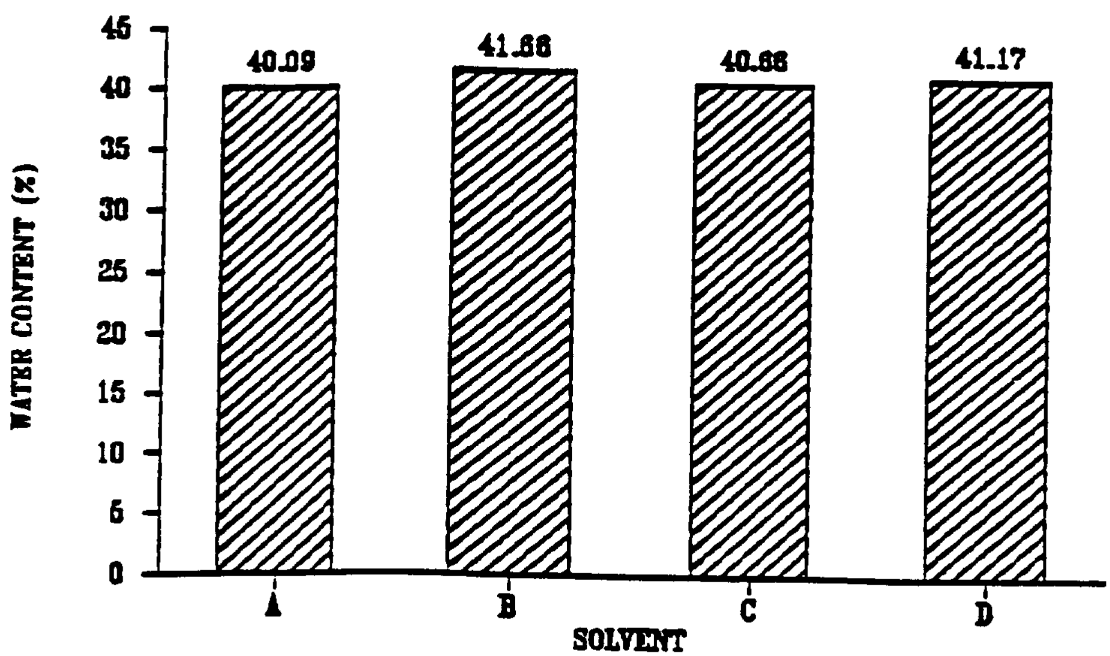
Type of diluent	RPD[1]	Water Content % (w/w) Average	Time to Endpoint (minutes)
a. 100% pyridine	2.05	40.09	10-29
b. 50% v/v methanol 50% v/v formamide	2.06	41.66	6
c. 100% methanol	0.64	40.66	9-13
d. 50% v/v methanol 50% v/v DMF	0.61	41.17	10

[1] RPD = Relative Percent Difference from Theoretical Value

Figure 7. Water content of a acrylic roofing material using ASTM D4017 with various solvent systems

FIGURE 7

WATER CONTENT of a Fire Retardant Acrylic Roofing Material by K.F. Titration using Varying Solvents



A) 100% PYRIDINE

B) 50% METHANOL / 50% FORMAMIDE (v/v)

C) 100% METHANOL

D) 50% METHANOL / 50% DMF (v/v)

Table 9. Water Content of a Wood Sealer, Using Various Solvent Systems

The Effect of Different diluents on the Water Content Determination of a Waterborne Wood Sealer

Type of diluent	RPD[1]	Water Content % (w/w) Average	Time to Endpoint (minutes)
a. 100% pyridine	0.77	79.48	3-4
b. 50% v/v methanol 50% v/v formamide	0.44	79.28	6
c. 100% methanol	0.51	78.47	4
d. 50% v/v methanol 50% v/v DMF	0.71	78.31	4

[1] RPD = Relative Percent Difference from Theoretical Value

Figure 8. Water content of a wood sealer using ASTM D4017 with various solvent systems

FIGURE 8

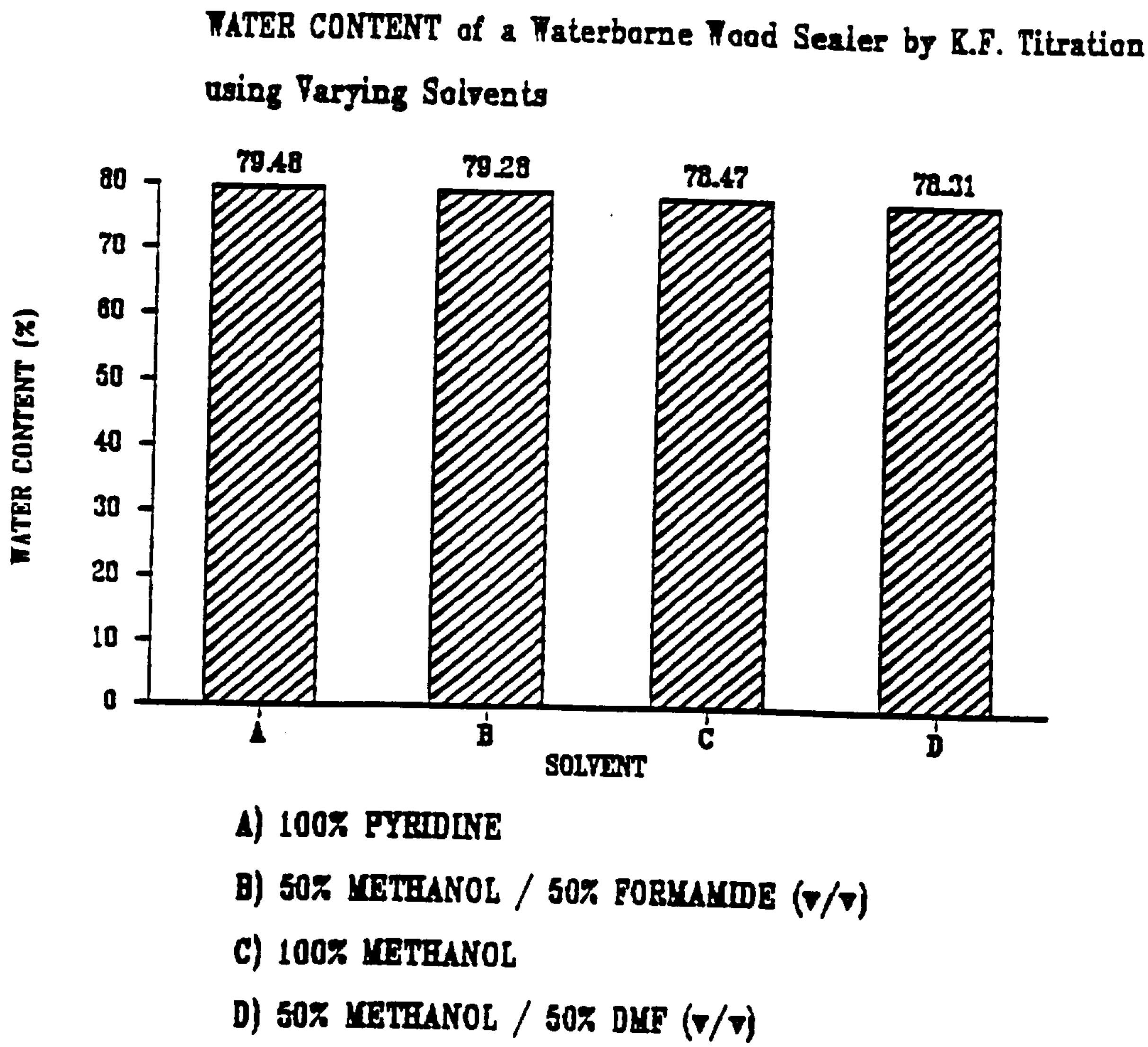


Table 10. Water Content of a Latex Coating Using Various Solvent Systems

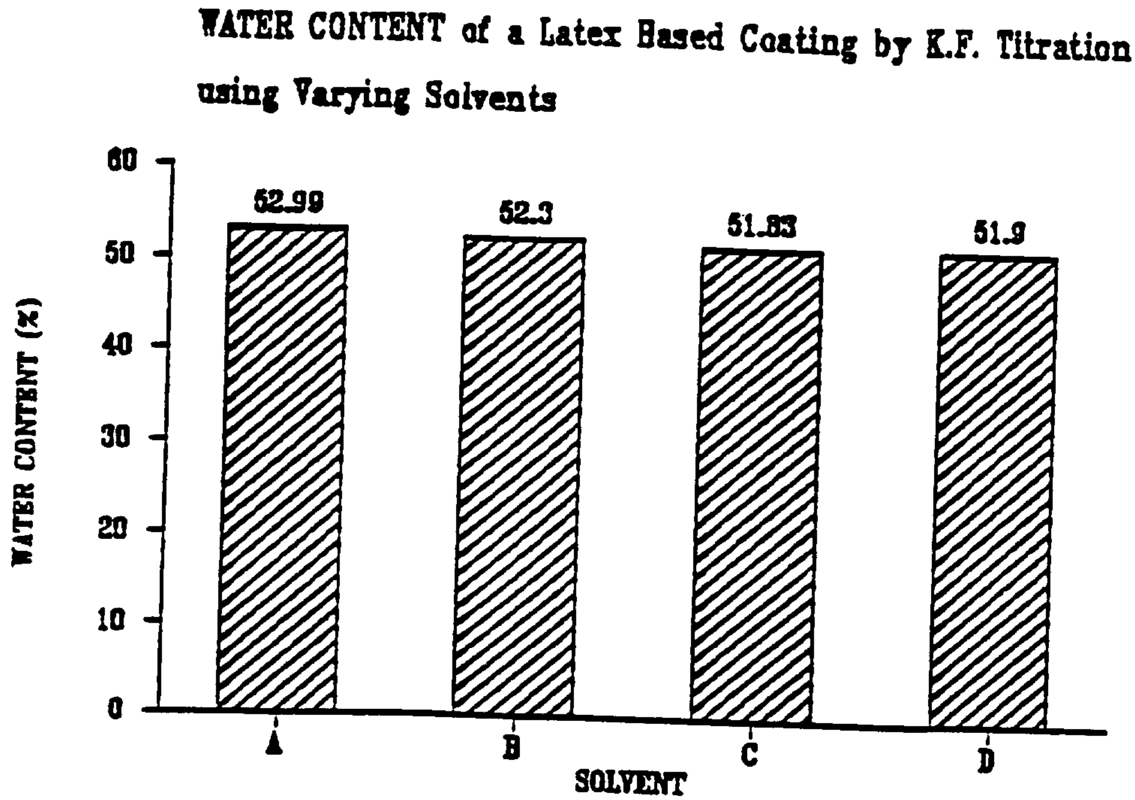
The Effect of Different Diluents on the Water Content Determination of a Latex Based Coating.

Type of diluent	RPD[1]	Water Content % (w/w) Average	Time to Endpoint (minutes)
a. 100% pyridine	1.40	52.99	5-6
b. 50% v/v methanol 50% v/v formamide	0.08	52.30	6
c. 100% methanol	0.83	51.83	5-6
d. 50% v/v methanol 50% v/v DMF	0.69	51.90	10

[1] RPD = Relative Percent Difference from Theoretical Value

Figure 9. Water content of a latex coating using ASTM D4017 with various solvent systems

FIGURE 9



A) 100% PYRIDINE

B) 50% METHANOL / 50% FORMAMIDE (v/v)

C) 100% METHANOL

D) 50% METHANOL / 50% DMF (v/v)

Table 11. Water Content of a Latex Coating Using Various Solvent Systems

The Effect of Different Diluents on the Water Content Determination of a Latex Based Coating.

Type of diluent	RPD[1]	Water Content % (w/w) Average	Time to Endpoint (minutes)
a. 100% pyridine	0.44	52.07	6-7
b. 50% v/v methanol 50% v/v formamide	-.10	51.79	8
c. 100% methanol	0.42	51.62	5-9
d. 50% v/v methanol 50% v/v DMF	0.06	51.87	7-8

[1] RPD = Relative Percent Difference from Theoretical Value

Figure 10. Water content of a latex coating using ASTM D4017 with various solvent systems

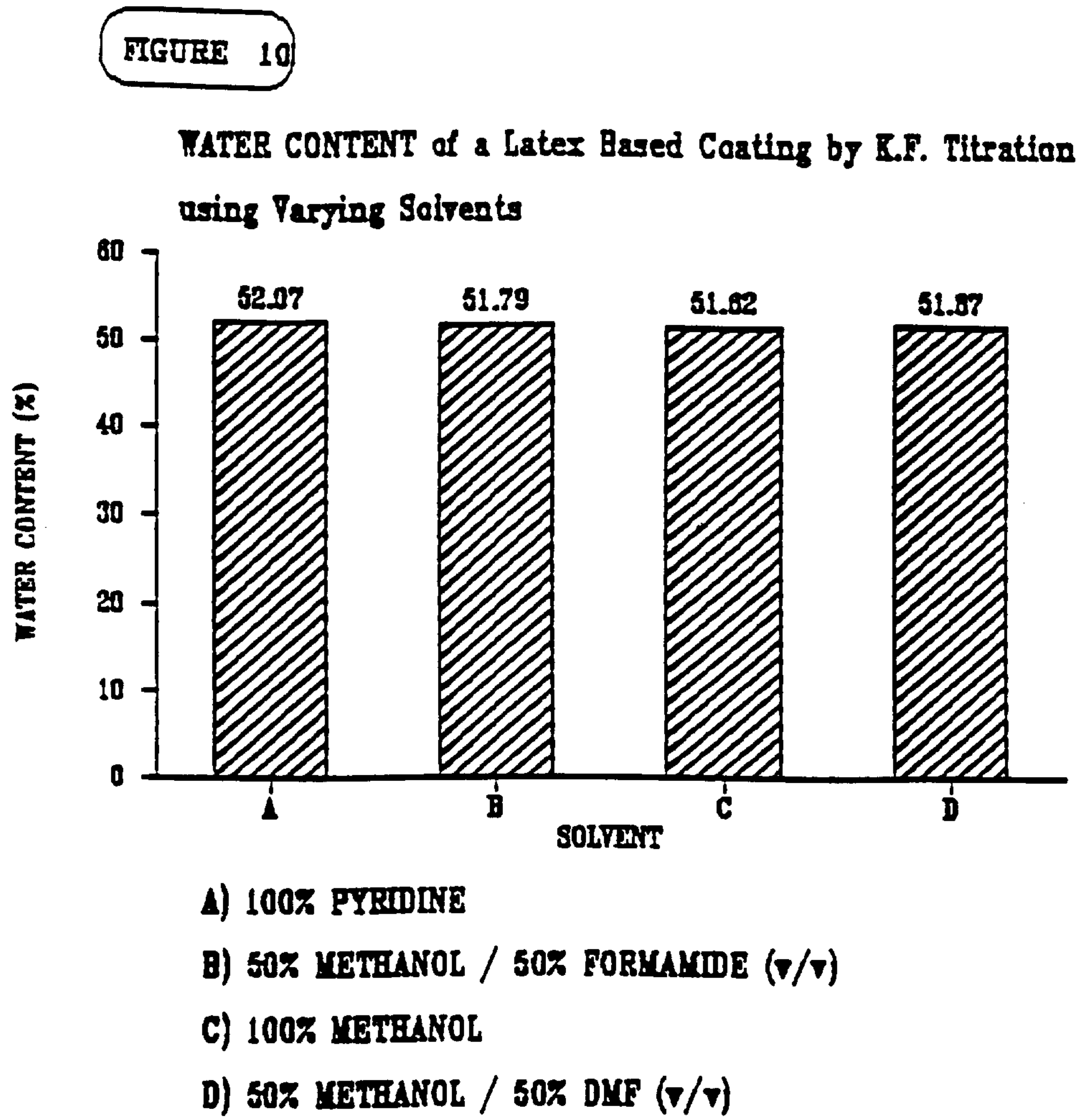


Table 12. The Effect of an Interfering Solvent (MEK) on Water Content Determination

The Effect of An Interfering Solvent (MEK) on the Water Content Determination using a Microprocessor controlled KF Titration with 100 Percent Methanol as Diluent

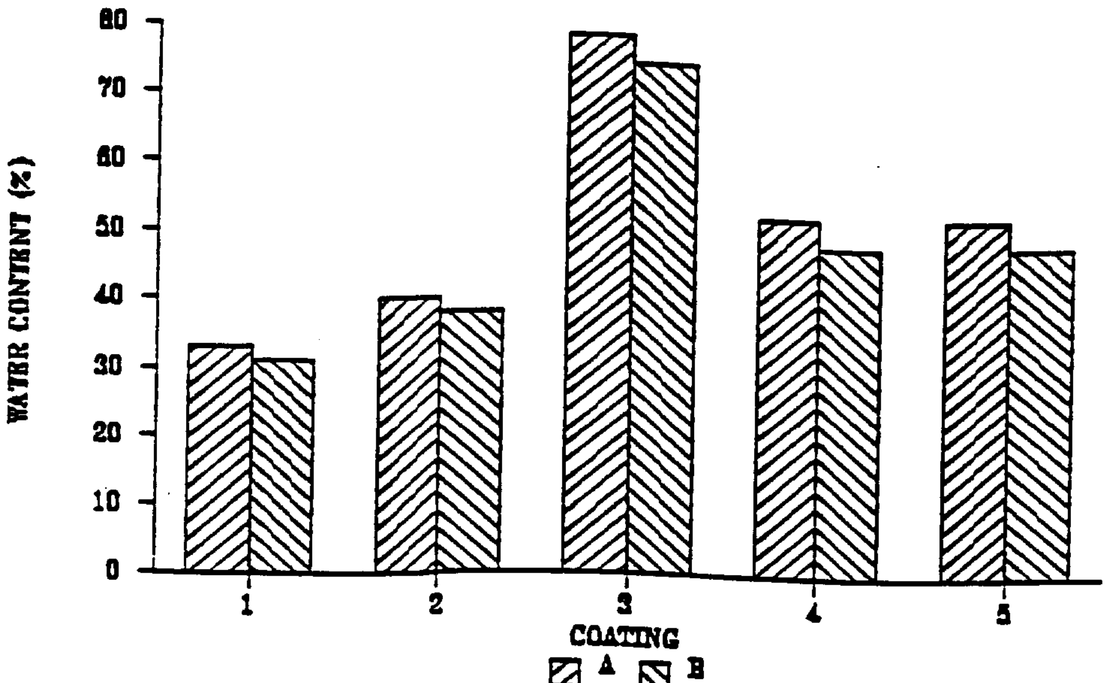
	Sample	Water Content spike level % (w/w)	Water Content % w/w)	RPD[1]	Endpoint (minutes)
1.	High-Build Waterborne Terpolymer	6.73	29.83	0.83	6-7
2.	Fire Retardant Acrylic Roofing material	8.45	38.09	1.59	12-15
3.	Water borne Wood Sealer	7.51	72.98	0.01	4-5
4.	Latex Based Coating	8.96	47.31	0.15	5-8

[1] RPD = Relative Percent Difference between theoretical corrected water content and that obtained with the MEK spike.

Figure 11. Effect of an Interfering solvent (MEK) on water content determination

FIGURE 11

The Effect of an Interfering Solvent (MEK) on the Water Content Determination using a Microprocessor Controlled K.F. Titrator w: 100% Methanol as Solvent



A) ORIGINAL (theoretical) WATER CONTENT

B) WATER CONTENT with MEK Interferent

1) High-Build Waterborne Terpolymer Coating

2) Fire Retardant Acrylic Roofing Material

C) Waterborne Wood Sealer

D) Latex Based Coating

E) Latex Based Coating

6. EXPERIMENTAL Volatile Organic Compounds-- Summary of Results Using Experimental Test Methods (ASTM D2369)

A. High Solids polyester/urethane coating

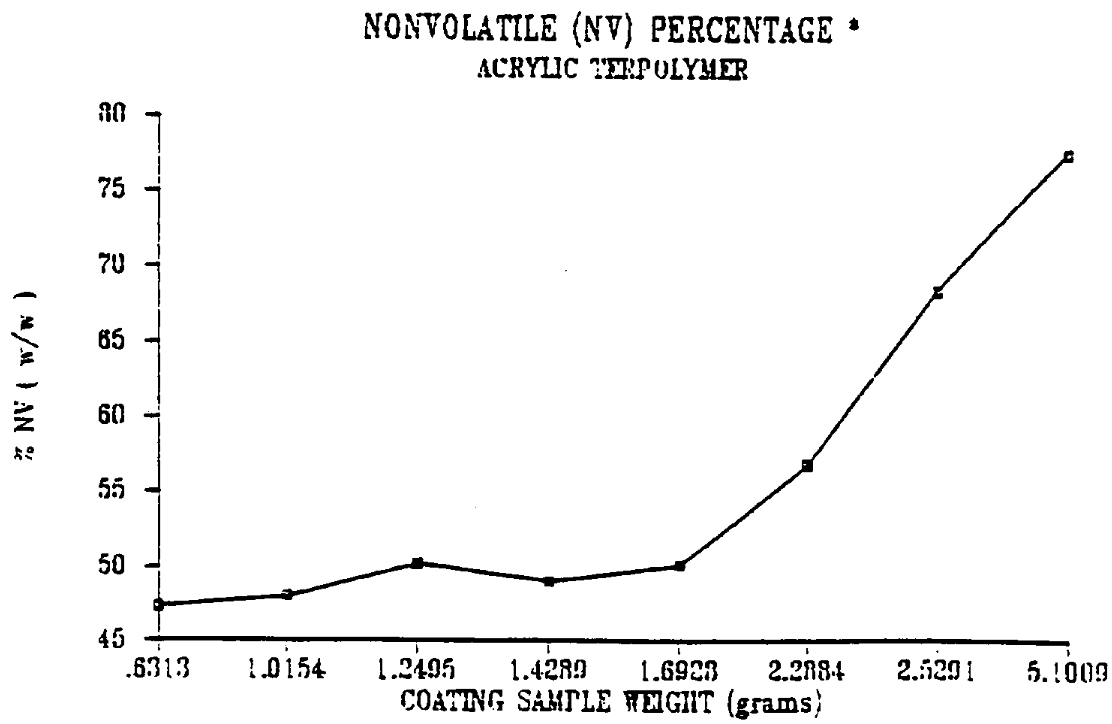
The proposed modification to ASTM D2369-87 of using dual thermocouples for monitoring the heated zones in a forced-air convection oven was used in developing the following information.

The volatile content of a three (3) component high-solids polyester/urethane coating was measured using four (4) different heating/induction methods. These results are given on page 48, **TABLE 13, Volatile Content of a High Solids polyester/urethane coating.**

The total non-volatile (NV) content of a water-borne acrylic terpolymer was measured using ASTM D2369. A variable which was introduced into the original ASTM specification was coating sample weight. The coating weight used varied from 0.63g to 5.1g. Coating sample size was introduced as a variable because some coating manufacturers use up to 5.0g when determining the total non-volatile (NV) content and consequently the VOC of their coating samples. The total NV of the acrylic terpolymer remained consistent (between 47 and 50 percent w/w) when 0.6 to 1.7g of sample was used. When 2.3 to 5.1g of sample was used the NV content increased dramatically (from 60 to 80 percent (w/w)). The numbers are given in Figure 12.

Figure 12. Non-Volatile content as a function of sample weight

FIGURE 12



* NONVOLATILE CONDITIONS USED WERE 110C FOR SIXTY (60) MINUTES

B. Discussion:

The total measured volatile content for the multiple component, high-solid polyester/urethane coating samples ranged widely. When 0.6g of mixed sample was used, the induction time whether one (1) or three (3) hours had little effect on the measured total volatile content (approximately 1.0% difference). Diluent was added during the induction period. The coating sample (0.6g) with no added diluent and a one (1) hour induction time at 77°F had a total volatile content four (4) percent less than the two samples with the diluent added. Another variable which must be taken into consideration is the type of diluent added. If the diluent is highly volatile it will evaporate faster, which will allow the various components to react more rapidly and more completely due to the closer proximity of the reaction sites on the organic molecules of each component, possibly lowering the measured total volatile content. If the diluents used are compounds such as glycol ethers which have a low vapor pressure (high boiling point) the total volatile content may be increased due to diluent keeping the reaction sites further apart.

When the gel coat method was used, ten (10)g of mixed sample were given a thirty (30) minute induction time. the total volatile content was approximately twenty-eight (28) percent less than the coating samples tested at 0.6g. This large difference may be due to the larger molar mass of each component allowing a more complete reaction/crosslinking to occur, binding the volatile components. The reactive diluent in this case is styrene which evaporates rapidly in thin films. While the Gel Coat method lowered the total volatile content significantly, it may not be representative of the coating amount actually applied to the substrate.

Therefore, we conclude that the Gel Coat method is an invalid way of measuring the volatile content of coatings applied in the field, <u>unless</u> the coating is equal to (16-21) mils DFT. The intended use of the polyester coating is for automotive refinishing, and the desired dry film thickness is only 2 to 3 mils.

Table 13. Volatile Content of High Solid Polyester/Urethane Coatings

Sample	Method	Method Conditions	Volatile Content % (w/w)
a.	Gel Coat	10g of mixed sample was given a thirty (30) minute induction period at 77°F, the sample was then heated at 160°C for sixty (60) minutes.	**9.74**
b.	ASTM D2369 1 hr ind. at 77°F	0.6g of mixed sample was given a one (1) hour induction at 77°F, the sample was then heated at 110°C for sixty (60) minutes (no diluent was added).[1]	**35.77**
c.	ASTM D2369 - proposed modification for multiple component coatings*	0.6g of mixed sample was added to diluent and given a one (1) hour induction at 77°f, then heated at 110°C for sixty (60) minutes.	**38.41**
d.	ASTM D2369 3 hr ind. at 77°F	0.6g of mixed sample was added to diluent and given a three (3) hour induction at 77°F, then heated at 110°C for sixty (60) minutes.	**37.53**

[1] diluent used was methyl ethyl ketone (MEK)

* This modification is currently being proposed by ASTM Committee D-01

C. Determination of Volatile Content of Waterborne Coatings using a Microwave versus a Convection Oven

1. Summary of Test Method:

The volatile content of twelve (12) waterborne coating samples was determined using the existing (unmodified) ASTM D2369 test procedure (0.5g with added diluent at 110°C for sixty (60) minutes.)

The volatile content of the same twelve (12) coatings was then determined using a microwave oven. The coating sample size used was approximately 0.5g and was dispersed in 3 mls of diluent (deionized water). The coating samples were then subjected to three (3) different power levels on the microwave oven. The heating schedule used is given in **TABLE 14 Volatile Content of Waterborne using Microwave and Convection Ovens.**

The types of waterborne coatings analyzed included:

1. Emulsions

   A. Terpolymer
   B. Vinyl/acrylic
   C. Styrene/acrylic (non-pigmented)
   D. Clear acrylic
   E. Opaque acrylic

2. Electrostatic primers

3. Flame retardant roof coatings

4. Waterborne varnishes

5. Clear wood preservatives

6. Silane systems

A comparison of the volatile content determinations using a convection oven versus a microwave for the above coating samples are given in **TABLE 14, Volatile Content of Waterborne coatings using Microwave and Convection ovens.**

Figure 13. Comparison of volatile content using microwave and convection oven

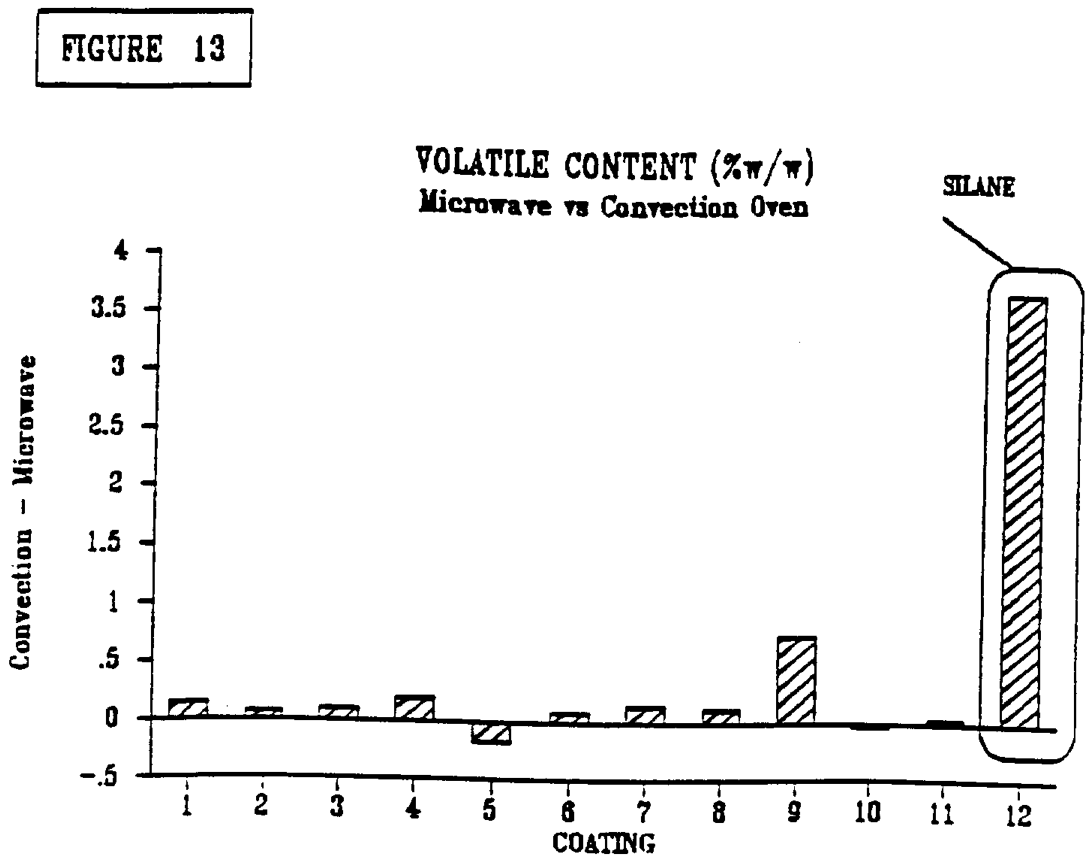
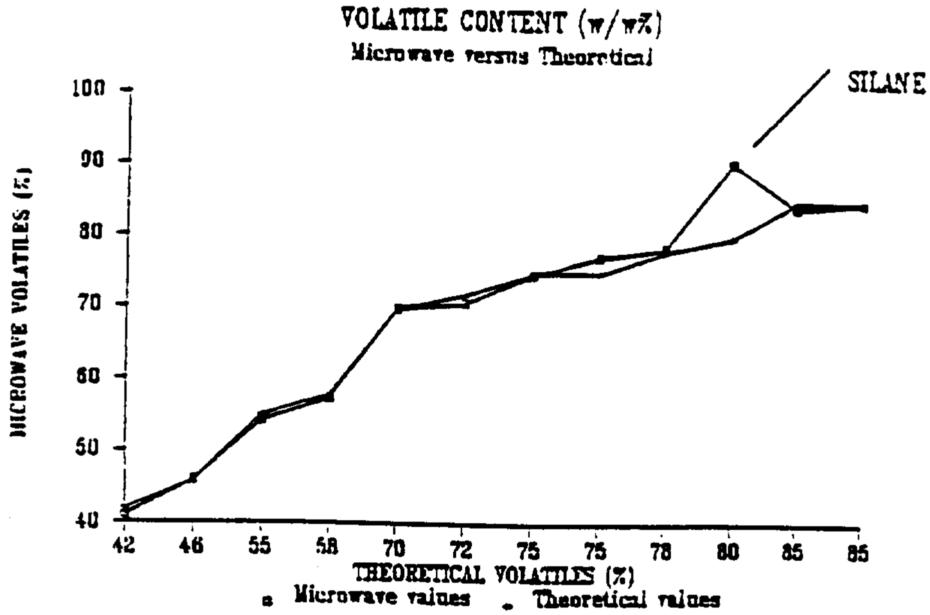
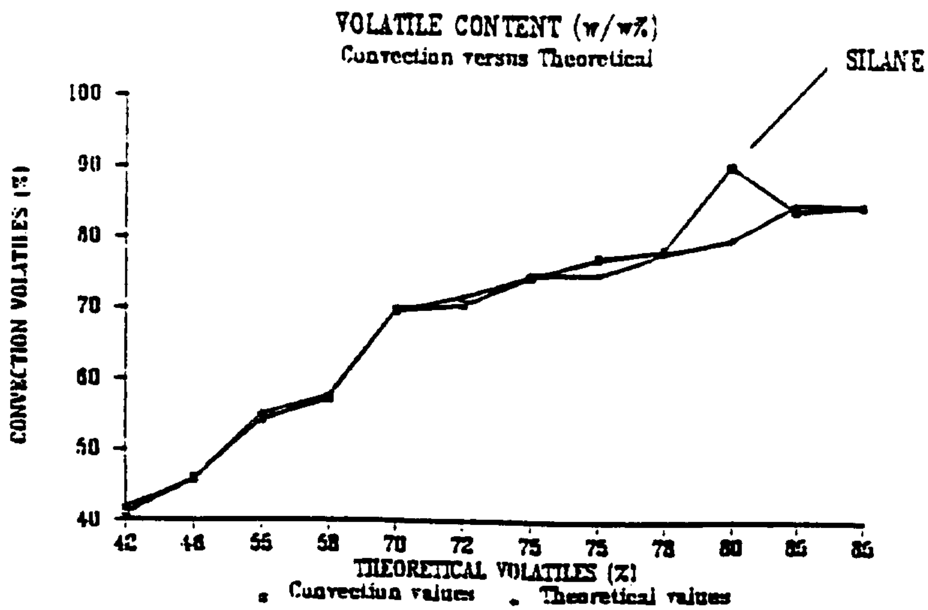


Figure 14. Volatile content using microwave and convection ovens as a function of total volatile content

FIGURE 14





Discussion:

D. Microwave versus Convection Oven

The total Volatile Content determined for the waterborne coating samples using the microwave oven are within 0.20% (w/w) of those obtained using the convection oven. A distinct advantage of using the microwave oven operated at the parameters given at the bottom of Table 14 is total time of an accurate analysis. An accurate volatile content for the waterborne systems studied can be obtained using the microwave oven in half the time of the convection oven (30 minutes versus 60).

E. Silane Systems

The measured total volatile content of one system deviated greatly from the theoretical value (90-93 versus 88). This deviation occurred using <u>both</u> types of ovens. The waterborne coating was the silane and the results obtained are given in Table 15.

The manufacturer of the silane* system provided reasons for such a large deviation in theoretical versus actual volatile organic content. The reasons given are as follows:

1. Alkylalkoxysilanes used as masonry water repellents react readily with the moisture in concrete when they are catalyzed by the highly alkaline concrete surface. Practically any acid or base will catalyze the silane/H_2O condensation reaction to give alcohol and a highly crosslinked silicone resin.

$$(RO)_3\ \text{Si-alkyl} \xrightarrow[\text{Organic Acid Catalyst}]{H_2O} (O)_{3/2}\ \text{Si-alkyl} + ROH$$

* Data supplied by silane manufacturer

2. Using ASTM D2369 with the oven at 110°C the normally non-volatile silane will evaporate giving extremely low values for percent solids.

3. The low values for percent solids under standard ASTM procedures are as a result of the tendency of uncatalyzed and uncondensed silane to evaporate at high temperatures instead of crosslinking which would normally occur at ambient temperatures.

4. The total volatile content of the silane system was then evaluated using a proposed acetic acid method supplied by the silane manufacturer using both microwave and convection ovens. The total volatile content measured using the convection ovens was 86.25 % (w/w) and 86.91 % (w/w) using the microwave oven, and both are within 1.75% (w/w) of the theoretical value. The total microwave heating time was thirty (30) minutes versus the sixty (60) minute using the convection oven. The microwave operating parameters used are given in **TABLE 14.**

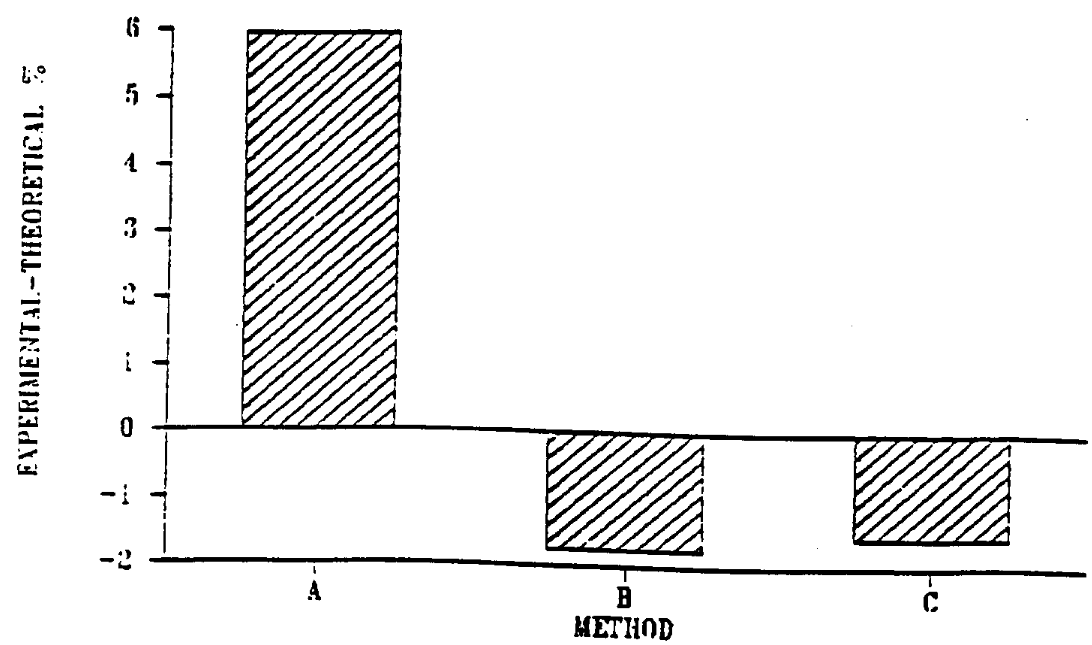
Discussion:

5. The conventional ASTM D2369 test procedure for measuring the total volatile content of silane based systems is inadequate due to uncondensed and uncatalyzed silane evaporating giving low total solid levels. Both the proposed acetic acid method and the ASTM proposed p-toluenesulfonic acid give total solids levels close to the theoretical values and may both viable, accurate methods for determining the total volatile content of these types of systems. A comparison of the total volatile content measured using the three (3) different methods is given in **TABLE 15** and displayed graphically in Figure 15.

Figure 15. Volatile content of silane systems using existing ASTM D2369 versus proposed methods

FIGURE 15

VOLATILE CONTENT OF SILANE SYSTEMS using conventional ASTM D2369, p-Toluenesulfonic acid (ASTM proposed method), and Acetic Acid method in a Convection Oven



A) ASTM D2369

B) Acetic Acid Method

C) p-Toluenesulfonic Acid (Proposed ASTM Method)

F. Determination of Volatile Content of Solvent Based Coatings using a Microwave Oven versus a Convection Oven

1. Single Component Systems

a. Summary of Test Method

The Total Volatile Content of three (3) types of single component systems were determined using both microwave and convection ovens with the existing ASTM D2369 test procedure. The coatings included a solvent based traffic paint (high solids), a lacquer (low solids) and a moisture cured polyurethane (low solids). The total volatile content for all three (3) coatings systems determined using the microwave oven were within 0.30% (w/w) of those measured using the convection oven. The microwave total heating time was thirty (30) minute and was sixty (60) minutes using the convection oven. The microwave operating parameters used are given in **TABLE 16.**

b. Discussion

The total volatile content of single component, solvent based coatings can be measured using a microwave with accurate results in half the time (30 minutes versus 60) of a convection oven. The volatile content numbers obtained using the microwave versus the convection oven are given in **TABLE 16** and displayed graphically in Figure 16.

2. Multiple Component System

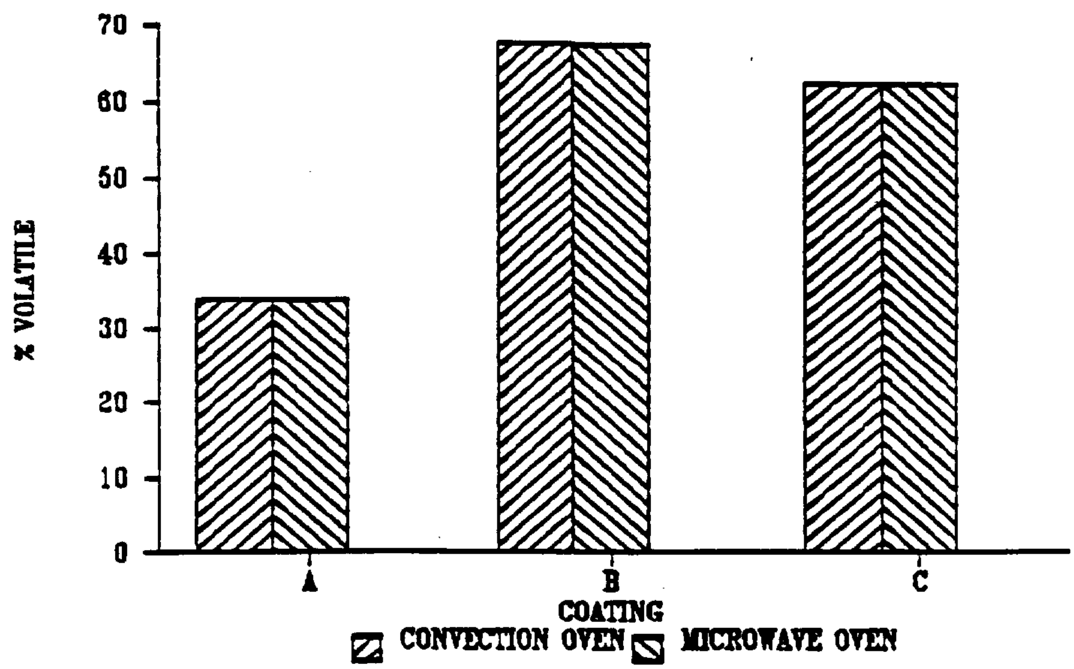
a. Summary of Test Method

The total volatile content of four (4) types of multiple component systems were determined using both convection and microwave ovens with the proposed ASTM test procedure. The volatile content of those systems was also measured introducing cure time as a variable using the microwave and convection ovens. The coatings included a three (3) component, aliphatic polyurethane, a high solids, two (2) component epoxy, a two (2) component epoxy mastic, and a two (2) component polyurethane.

Figure 16. Volatile content of a single component solvent based coating using convection and microwave ovens

FIGURE 16

VOLATILE CONTENT of Single Component Solvent Based Coatings using ASTM D2369 with Convection and Microwave Ovens



A) Traffic Paint (high solids)

B) Lacquer (low solids)

C) Moisture Cured Polyurethane (low solids)

The total volatile content of the two (2) component epoxy using the proposed ASTM test procedure was 6.36% (w/w) using the convection oven and 3.40% (w/w) using the microwave. No induction time using the convection oven resulted in a volatile content of 6.84% (w/w) and 8.56% (w/w) using the microwave. A twenty-four (24) hour at 77°F curing period (no heat applied) gave a volatile content of 2.51% (w/w). Heating the sample which was cured at 77°F for twenty-four (24) hours at 110°oC for sixty (60) minutes resulted in a total volatile content of 4.65% (w/w) using the convection oven and 4.91% (w/w) using the microwave (three (3) power levels used, not heated at 110°C).

The total volatile content of the epoxy mastic using the proposed ASTM test procedure was 10.10% (w/w) using the convection oven and 10.78% (w/w) using the microwave. No induction time using the convection oven resulted in a volatile content of 11.32% (w/w) and 10.32% (w/w) using the microwave. A twenty-four (24) hour at 77°F curing period (no heat applied) gave a volatile content of 11.64% (w/w) using the microwave (three (3) power levels used, not heated at 110°C).

The total volatile content of the three (3) component aliphatic polyurethane using the proposed ASTM test procedure was 27.25% (w/w) using the convection oven and 20.60% (w/w) using the microwave. No induction time using the convection oven resulted in a volatile content of 28.00% (w/w) and 11.87% (w/w) using the microwave. A twenty-four (24) hour at 77°F curing period of (no heat applied) gave a volatile content of 12.81% (w/w). Heating the sample which was cured at 77°F for twenty-four (24) hours at 110°C for sixty (60) minutes resulted in a total volatile content of 27.05% (w/w0 and 16.28% (w/w) using the microwave (three (3) power levels used, not heated at 110°C).

The total volatile content of the two (2) component polyurethane using the proposed ASTM test procedure was 49.50% (w/w) using the convection oven and 48.26% (w/w) with the microwave. No induction time using the convection oven resulted in a volatile content of 49.92% (w/w) and 48.46% (w/w) with the microwave. A twenty-four (24) hour at 77°F curing period (no heat applied) gave a volatile content of 46.81% (w/w). Heating the sample which was cured at 77°F for twenty-four (24) hours at 110°C for sixty (60) minutes resulted in a total volatile content of 49.69% (w/w) and 48.32% (w/w) using the microwave (three (3) power levels used, not heated at 110°C).

b. Discussion

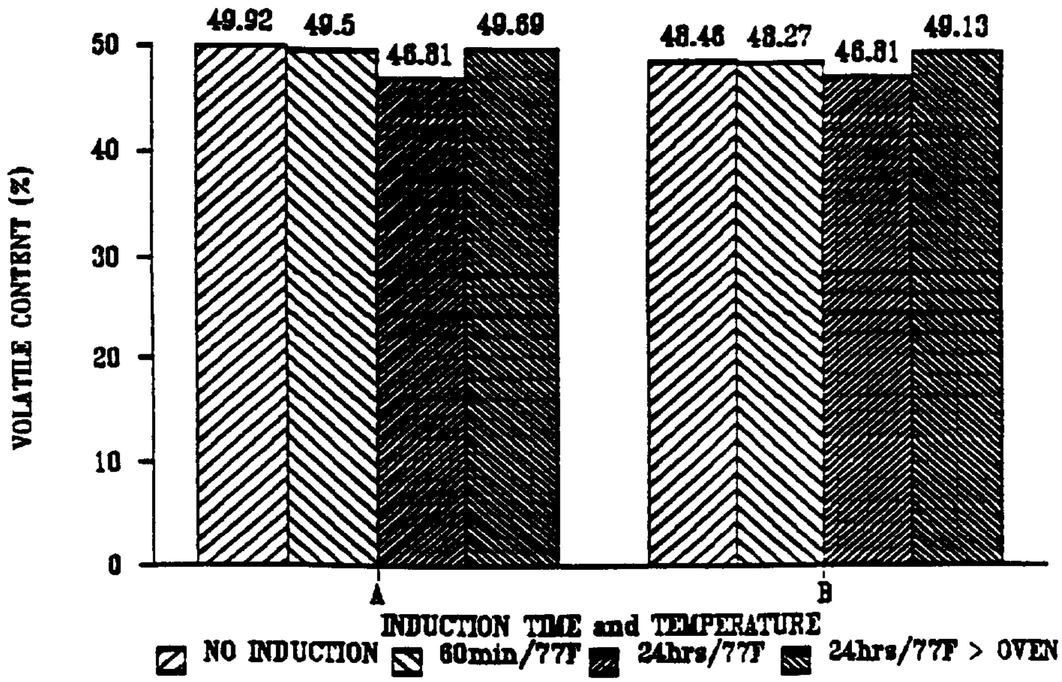
The total volatile content measured using the microwave and convection oven with proposed ASTM test procedure varied somewhat. The total volatile content measured for the epoxy were 3.40% and 6.35%, respectively while those measured for the epoxy mastic were within 0.18.5 (w/w). The total volatile content for the three (3) component polyurethane varied greatly. The microwave oven yielded a volatile content of 20.60% (w/w) and the convection oven 27.25% (w/w). The total volatile content measured for the two (2) component polyurethane were 48.26% and 49.50/5 (w/w), respectively.

The total volatile content of the two (2) component polyurethane coating was measured varying the amount of diluent and curing schedules with both microwave and convection ovens. The use of no diluent produced a lower volatile content with both the microwave and convection ovens using all curing schedules. These volatile content numbers on given in **TABLE 19** and displayed graphically in Figure 17. When the ASTM proposed testing procedure (one (1) hour induction at 77°F) was held constant, using no diluent resulted in a large deviation (8.86 Relative Percent Difference (RPD)). Adding three (3) mls diluent lowered the RPD to 2.40 between the microwave and convection measurements.

Figure 17. Volatile content of a two component polyurethane using microwave and convection ovens as a function of induction time

FIGURE 17

VOLATILE CONTENT OF A TWO COMPONENT POLYURETHANE USING MICROWAVE AND CONVECTION OVENS AS A FUNCTION OF INDUCTION TIME



A) INDUCTION TIME AND TEMPERATURE FOLLOWED BY 60 MINUTES @ 110C

B) INDUCTION TIME AND TEMPERATURE FOLLOWED BY MICROWAVE HEATING

The numbers obtained are given in **TABLE 18**. Amount of diluent, sample size, and induction temperature/time are the variables which affect the determination of the total volatile content of a coating sample the greatest. Reproducible, accurate, results can be obtained using a microwave oven in half the total time of analysis using the conventional convection oven. Some coating systems such as the three (3) component aliphatic polyurethane coating result in lower total volatile content when using the proposed ASTM test procedure with the microwave oven.

Table 14. Volatile Content of Waterborne Coatings Using Microwave and Convection Ovens

Coating type	Convection[1]	RPD[3]	Microwave[2]	RPD[3]	Theoretical
	Volatile Content % (w/w)				
1. Emulsions					
A) Terpolymer	46.17	0.37	46.02	0.04	46.00
B) Vinyl/acrylic	57.46	0.93	57.39	1.05	58.00
C) Styrene/acrylic	54.25	1.37	54.15	1.56	55.00
D) Clear acrylic	78.64	0.82	78.44	0.56	78.00
E) Opaque acrylic	69.97	0.04	70.14	0.20	70.00
2. Primers					
A) Electrostatic	74.90	0.13	74.81	0.25	75.00
B) Clear Sealers	84.26	0.87	84.11	1.05	85.00
C) Pigmented	85.00	0.00	84.88	0.14	85.00
3. Flame Retardant Roof Coating	41.86	0.33	41.11	2.14	42.00
4. Waterborne Varnish	70.77	1.72	70.80	1.68	72.00
5. Clear Wood Preservative	77.34	1.53	77.30	3.02	75.00
6. Silane System	93.95	6.54	90.28	2.56	88.00

[1] Convection: Samples were analyzed in triplicate according to the existing ASTM D2369 test procedure (0.5g sample, 3 mls diluent (water) at 110°C for sixty (60) minutes.
[2] Microwave*: Samples were analyzed in triplicate.
[3] RPD - Relative Percent Difference between measured and theorectical value.

Test parameters:

A. Sample size: 0.5g
B. Sample dish: High density polyethylene weighing boats on a glass carousel
C. Heating schedule:
   1. Low (approx. 150 watts) - 10 minutes
   2. Medium (approx. 450 watts) - 10 minutes
   3. Medium - High (approx. 600 watts) - 10 minutes

* Microwave oven has been modified through the use of a metal shroud with forced ventilation to reduce risk of fire with flammable organic vapors.

Table 15. Volatile Content of Waterborne Silane System Using Microwave and Convection Ovens

Coating type	Convection[1]	RPD[3]	Microwave[2]	RPD[3]	Theoretical
	Volatile Content % (w/w)				
A. Conventional ASTM D2369	46.17	0.37	46.02	0.04	78.00
B. Proposed Acetic Acid Method	54.25	1.37	54.15	1.56	78.00
C. Proposed ASTM Test Method using p-toluene sulfonic acid	78.64	0.82	78.44	0.56	78.00

[1] Convection: Samples were analyzed in triplicate 0.5g sample sixty (60) minutes).

[2] Microwave*: Samples were analyzed in triplicate.

[3] RPD - Relative Percent Difference between measured and theorectical value.

Test parameters:

A. Sample Size: 0.5g

B. Sample dish: High density polyethylene weighing boats on a glass carousel.

C. Heating schedules:

1. low (approx. 150 watts) - 10 minutes
2. Medium (approx. 450 watts) - 10 minutes
3. Medium - High (approx. 600 watts) - 10 minutes

* Microwave oven has been modified through the use of a metal shroud with forced ventilation to reduce risk of fire with flammable organic vapors.

Table 16. Volatile Content of Single Component, Solvent Based Systems using a Microwave and Convection Ovens

Coasting Type	Volatile Content % (w/w) Convection[1]	Microwave[2]	RPD[3]
A. High Solids traffic paint (high solids)	33.91	33.82	0.13
B. Lacquer (low solids)	67.74	67.49	0.37
C. Moisture cured polyurethane (low solids)	37.52	37.42	0.16

[1] Convection: Samples were analyzed in triplicate according to ASTM D2369 test procedure (0.5g sample, 3ml diluent and heated at 110°C for sixty (60) minutes).

[2] Microwave*: Samples were analyzed in triplicate.

[3] RPD - Relative Percent Difference between measured and theorectical value.

Test parameters:

A. Sample Size: 0.5g

B. Sample dish: Glass petri dishes on a glass carousel.

C. Heating schedules:

1. Low (approx. 150 watts) - 10 minutes
2. Medium (approx. 450 watts) - 10 minutes
3. Medium - High (approx. 600 watts) - 10 minutes

* Microwave oven has been modified through the use of thermocouples and a metal shroud with forced ventilation to reduce risk of fire with flammable organic vapors.

Table 17. The Effect of Diluent on the Volatile Content of a Single Component Polyurethane

The Effect of Diluent on the Total Determination of the Volatile Content of a Single Component, Moisture Cured Polyurethane

	Convection Oven*
Diluent Added (mls)	**Volatile Content (% w/w)**
0	37.41
2	38.06
4	38.10
6	38.27

* All coating sample were given one (1) hour induction time at 77°F prior to heating at 110°C for sixty (60) minutes.

Table 18. Total Volatile Content of Multi-Component Systems, Microwave vs. Convection Oven, 3 ml Diluent

Coating	Induction	Convection[1]		Microwave[2]	RPD[3]
A) Two (2)	1) 1 hr @ 77°F	6.35		3.40	60.51
Component	2) 0 hrs @ 77°F	6.84		8.56	
Epoxy	3) 24 hrs @ 77°F	--	2.51	--	
B) Two (2)	1) 1 hr @ 77°F	10.10		10.28	1.77
Component	2) 0 hrs @ 77°F	11.32		10.32	
Epoxy	3) 24 hrs @ 77°F	--	9.80	--	
Mastic	4) 24 hrs @ 77°F	12.61		12.03	
C) Three (3)	1) 1 hr @ 77°F	6.35		3.40	60.51
Component	2) 0 hrs @ 77°F	6.84		8.56	
polyurethane	3) 24 hrs @ 77°F	--	2.51	--	
D) Two (2)	1) 1 hr @ 77°F	10.10		10.28	1.77
Component	2) 0 hrs @ 77°F	11.32		10.32	
polurethane	3) 24 hrs @ 77°F	--	9.80	--	

1 Sample were analyzed in triplicate (0.5g sample sixty (60) minutes at 110°C).
2 Microwave*: Samples were analyzed in triplicate.

Test parameters:

A. Sample Size: 0.5g

B. Sample dish: Glass petri dishes on a glass carousel.

C. Heating schedules:
   1. Low (approx. 150 watts) - 10 minutes
   2. Medium (approx. 450 watts) - 10 minutes
   3. Medium - High (approx. 600 watts) - 10 minutes

* Microwave oven has been modified through the use of thermocouples and a metal shroud with forced ventilation to reduce risk of fire with flammable organic vapors.

3 RPD - Relative Percent Difference between measured and theorectical value.

4 Samples were then subjected to either convection only at 110°C for sixty (60) minutes or microwave for thirty (30) minutes.

Table 19. Effect of Diluent on the Total Volatile Content, 2-Component Polyurethane Coating, using Microwave and Convection Ovens

Diluent added mls	RPD[3]	Convection[1]	Microwave[2]
0	8.86	47.87	43.04
3	2.40	49.50	48.27

1 Convection oven conditions consisted of a one (1) hour induction at 77°F then sixty (60) at 110°C.

2 Microwave - samples were given a one (10 hour induction at 77°F prior to heating schedule given in **TABLE 15.**

3 RPD = Relative Percent Difference

Table 20. The Effect of Induction Time and Temperature on Volatile Content of a 2-Component Polyurethane Microwave and Convection Ovens, 3 ml Diluent

Diluent added mls	RPD[3]	Convection[1]	Microwave[2]
1. No induction[4]	8.86	47.87	43.04
2. Sixty (60) hours at 77°F	2.40	49.50	48.27
3. Twenty-four (24) hours at 77°F[4]	--	46.81	46.81
4. Twenty-four (24) hours at 77°F[4]	1.11	49.69	49.13

1 Convection samples were analyzed in triplicate

2 Microwave heating schedule used in given at the bottom of TABLE 18.

3 RPD = Relative Percent Difference

4 Samples were then subjected to sixty (60) minutes at 110°C using the convection oven or thirty (30) minutes using the microwave.

G. Determination of Volatile Content of a Solvent-Based, Two Component Polyurethane coating using Sample Weight versus Ambient Cure (24 hours) and Ambient Cure (24 hours) plus 110°C for 60 minutes.

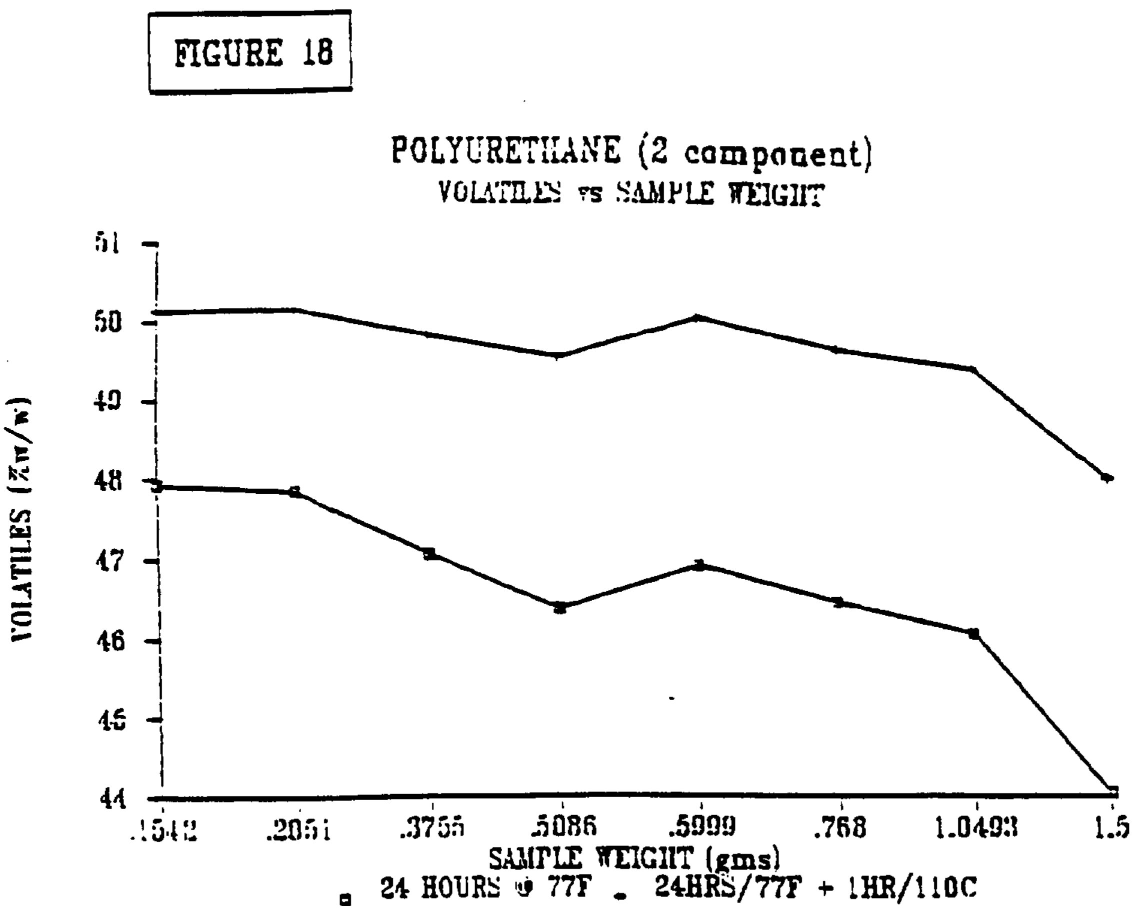
1. Summary of Test Method

The coating sample size of the polyurethane coating varied from 0.15g to 1.5g of the premixed components placed in three (3) mls of xylene. The total volatile content using the different sample weights were measured after an ambient cure of twenty-four (24) hours at 77°F. The samples were then heated at 110°C for sixty (60) minute and the volatile content remeasured.

2. Discussion:

Overall, the lowest sample size used during the ambient cure (24 hours at 77°F gave the highest volatile content (47.92% (w/w) for 0.1g versus 44.05% (w/w) using 1.5g). The same general trend was true after heating the sample at 110°C for sixty minutes, but the spread was lower (50.13% (w/w) versus 48.07% w/w, respectively). The samples which were heated at 110°C for sixty (60) minutes resulted in a higher volatile content of 50.13% (w/w) versus 47.92% (w/w) measured for the samples which were not heated using the 0.15g of sample. These numbers are given in **TABLE 21. Determination of Volatile of a Solvent-Based Two (2) Component Polyurethane Coating using Different Sample Weights** and displayed graphically in Figure 19.

Figure 18. Volatile content of a two component polyurethane as a function of sample weight



H. Determination of Volatile Content of a Solvent-Based Single Component Moisture Cured Urethane Coating using Sample Weight versus Ambient Cure (24 hours) plus 110°C for 60 minutes.

1. Summary of Test Method:

The coating sample size of the moisture cured urethane coating varied from 0.11g to 1.42g placed in three (30 mls of xylene. The total volatile contents using the different sample weights were measured after an ambient cure of twenty-four (24) hours at 77°F. The samples were then heated at 110°C from sixty (60) minutes and the volatile content remeasured.

2. Discussion:

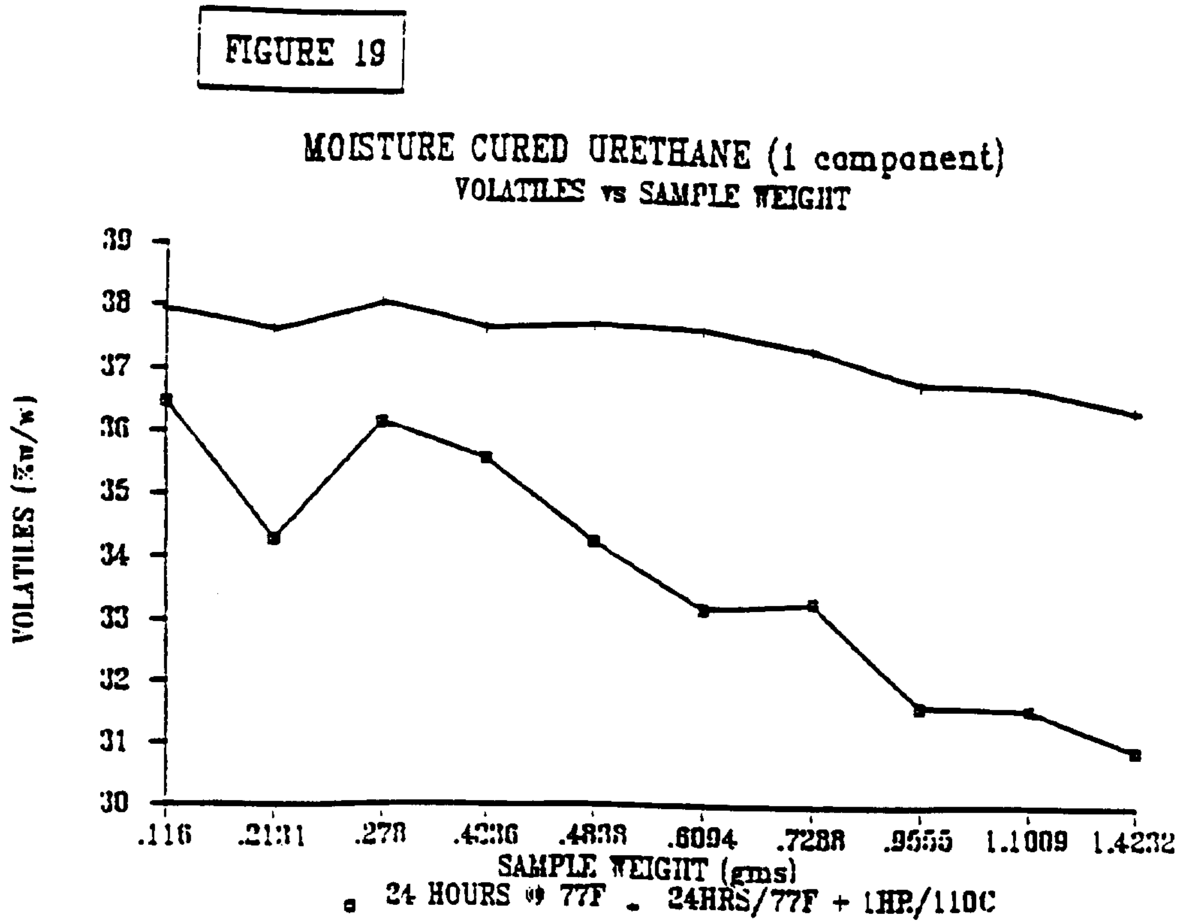
Overall, the lowest sample size used during the ambient cure (24 hours at 77°F) gave the highest volatile content (36.47% (w/w) for 0.11g versus 30.92% (w/w) using 1.4g). A similar pattern was observed after heating the sample at 110°C for sixty (60) minutes, but the spread was lower (37.93% (w/w) versus 36.41% (w.w), respectively). The samples which were heated at 110°C for sixty (60) minutes resulted in a higher volatile Content of 37.93% (w/w) versus 36.47) for the samples which were not heated using the 0.11g of coating sample. These numbers are given in **TABLE 22, Determination of Volatile Content of a Solvent-Based Single Component Moisture Cured Urethane Coating using Different Sample Weights** and displayed graphically in Figure 20.

I. Determination of Volatile Content of a Solvent-Based Single Component Acrylic Enamel using Sample Weight versus Ambient Cure (24 hours) plus 110°C for 60 minutes.

1. Summary of Test Method:

The coating sample size of the acrylic coating varied form 0.12g to 1.3g of the coating placed in three (3) mls of xylene. The total volatile content using the different sample weights were measured after an ambient cure of twenty-four (24) hours at 77°F. The samples were heated at 110°C for sixty (60) minutes and the volatile content remeasured.

Figure 19. Volatile content of a single component urethane as a function of sample weight



2. Discussion:

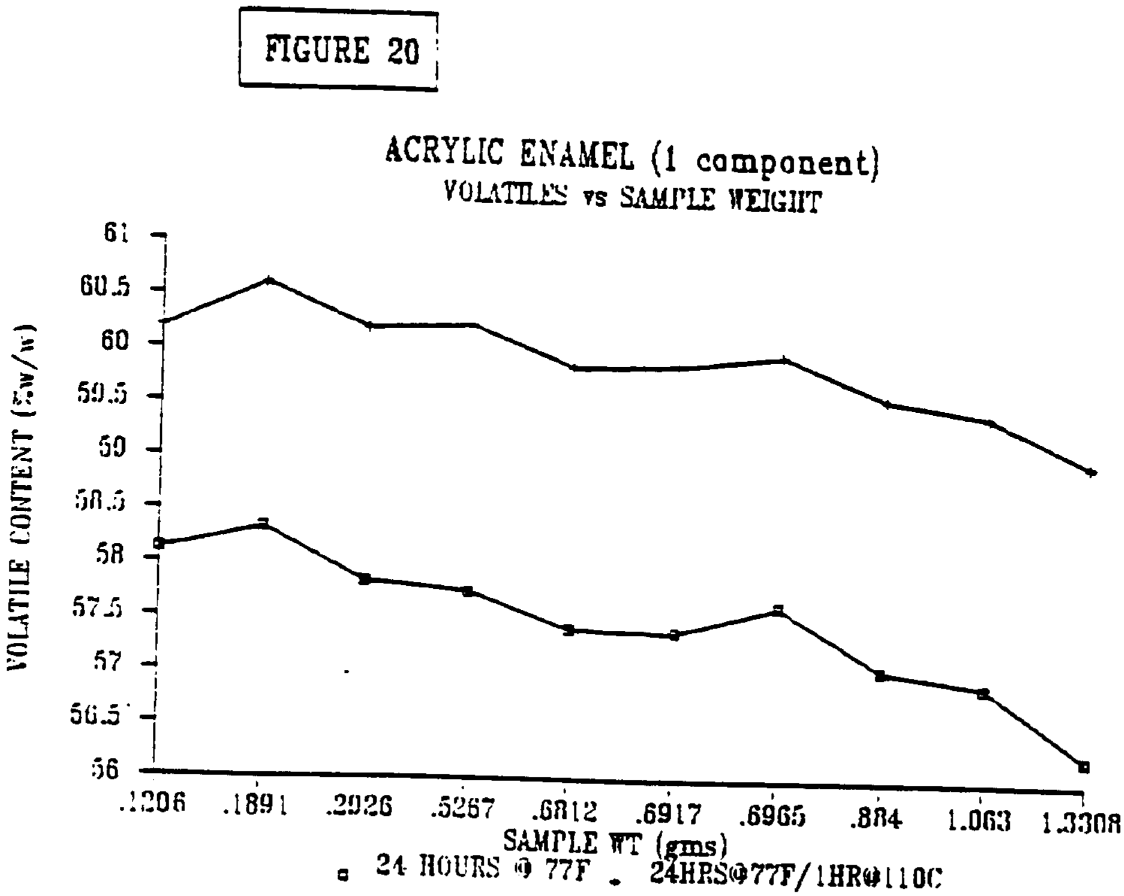
Overall, the lowest sample size used during the ambient cure (24 hours at 77°F) gave the highest volatile content (58.13% (w/w) for 0.12g versus 56.24% (w/w) using 1.3g) A similar pattern was observed after heating the sample at 110°C for sixty (60) minutes, but the spread was lower (60.20% (w/w) versus 59.01% (w/w), respectively). The sample which were heated at 110°C for sixty (60) minutes resulted in a higher volatile content of 60.20% (w/w) versus 58.13% (w/w) measured for the samples which were not heated using the 0.12g of sample. These numbers are given in **TABLE 24. Determination of Volatile Enamel using Different Sample Weights** and displayed graphically in FIGURE 20.

J. Determination of Volatile Content of a Solvent-Based Two Component Polyurethane coating using Manufacturer's Spreading Rate versus Long-Term Ambient Cure.

1. Summary of Test Method

The manufacturer's recommended spreading rate for the coating was 610 ft^2/gal which is equivalent to 0.157g of wet coating in an aluminum dish. Keeping the sample weight constant, using no induction time, the coating was cured at 77°F for twenty-four (24) hours, and 77°F for forty-eight (48) hours and the volatile content measured. The coatings which were cured forty-eight (48) hours at 77°F were then heated at 110°C for sixty (60) minutes and the volatile content remeasured. The sample weights were then varied between 0.15g and 0.50g, given a one (1) hour induction time, and then subjected to the same curing schedules as the samples which were cured with no induction time. The volatile content was then measured. The sample weights were also varied and the coatings given a two (2) hour induction time and then subjected to the same curing schedules as the samples which were cured with no induction time.

Figure 20. Volatile content of a single component enamel as a function of sample weight



2. Discussion:

Using 0.15g of sample with no induction time cured at 77°F for twenty-four (24) hours resulted in the lowest volatile content 47.80% (w/w) while the sample which was heated at 110°C for sixty (60) minutes resulted in the highest 49.45% (w/w). A similar pattern was observed for the samples which were subject to one (1) and two (2) hour induction times. The highest sample weight resulted in the lowest volatile content numbers. Overall, no induction time (keeping sample weight of 0.15g and cure of 24 at 77°F constant) resulted in the highest volatile content of 47.80% (w/w) and the two (2) hour induction period the lowest 37.20% (w/w). These numbers are given in **TABLE 24. Determination of Volatile Content of a Solvent-Based Two (2) Component Polyurethane Coating using Manufacturer's Recommended Spreading Rate versus Long-Term Ambient Cure,** and displayed graphically in FIGURES 21 and 22.

K. Determination of Volatile Content of a Solvent-Based Single Component Moisture Cured Urethane Coating using Manufacturer's Recommended Spreading Rate versus Long-Term Ambient Cure.

1. Summary of Test Method

The manufacturer's recommended spreading rate for the coating was 238 ft^2/gal which is equivalent to 0.38g of wet coating in an aluminum dish. Keeping the sample weight constant, the coating was cured at 77°F for twenty-four (24) hours, and 77°F for forty-eight (48) and seventy-two (72) and one hundred forty-four (144) hours and the volatile content measured. The coatings which were cured seventy-two (72) hours at 77°F were then heated at 110°C for sixty (60) minutes and the volatile content remeasured.

2. Discussion:

Lowest sample weight 0.3809g gave the highest Volatile content 36.23% (w/w) and correspondingly the highest sample weight (0.458g) gave the lowest volatile content of 35.48% (w/w). It appears that the longer the samples are cured at ambient temperature, the higher the volatile content measured using all sample size weights. The samples which were heated at 110°C for sixty (60) minutes after a seventy-two (72) hour ambient cure resulted in the highest volatile content measured 38.15% (w/w) using 0.3809g. These numbers are given in **TABLE 25. Determination of Volatile content of a Solvent-Based Moisture Cured Urethane Coating using Manufacturer's Spreading Rate versus Long-Term Ambient Cure** and displayed graphically in FIGURES 23, 24 and 25.

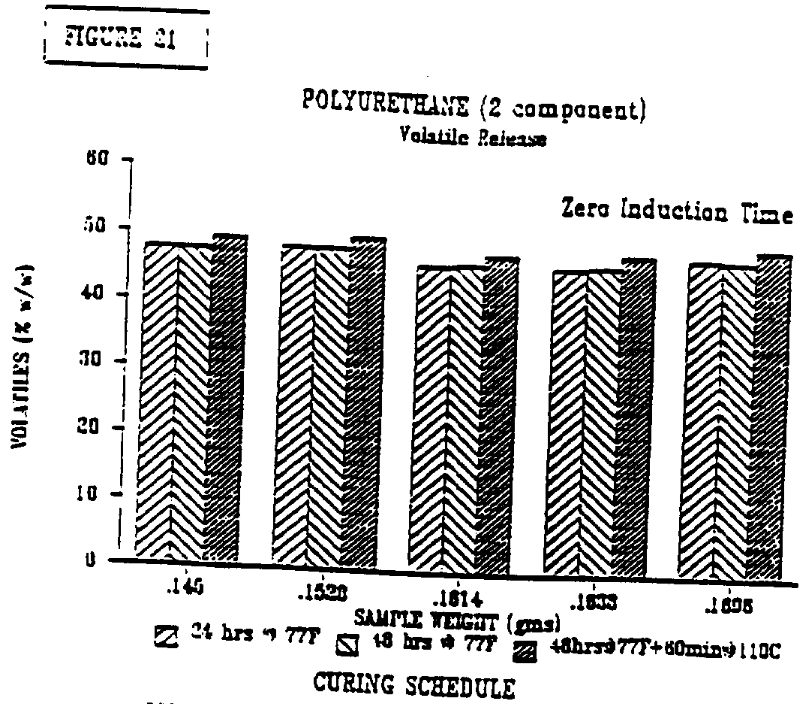
Table 21. Volatile Content of a 2-Component Polyurethane Coating Using Different Sample Weights

Sample Wt. grams	24 hour Cure at 77°F	24 hour cure at 77°F + 110°C for 60 minutes
0.1542	47.92	50.13
0.2051	47.88	50.17
0.3755	47.08	49.85
0.5086	46.38	49.57
0.5999	46.94	50.09
0.7690	46.46	49.70
0.0493	46.07	49.45
0.5000	44.05	48.07

Table 22. Volatile Content of a Single-Component Solvent-Based Moisture-Cured Urethane Coating Using Different Sample Weights

Sample Wt. grams	24 hour Cure at 77°F	24 hour cure at 77°F + 110°C for 60 minutes
0.1160	36.47	37.93
0.2131	34.30	37.63
0.2180	36.15	38.06
0.4236	35.58	37.65
0.4838	34.25	37.70
0.6094	33.21	37.66
0.7288	33.32	37.35
0.9555	31.63	36.82
1.1009	31.57	36.76
1.4232	30.92	36.41

Figure 21. Volatile content of a two component polyurethane as a function of induction time



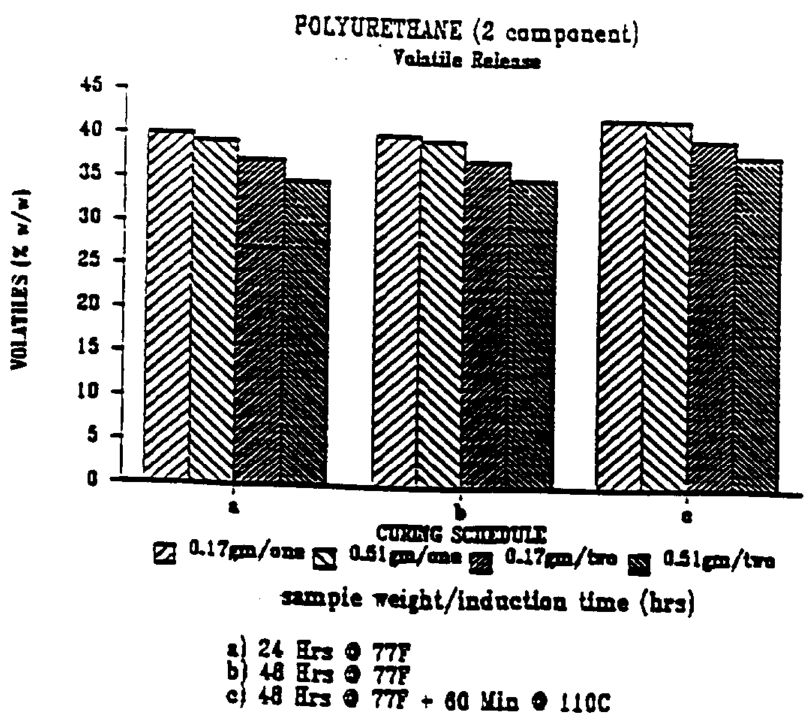


Figure 22. Additional volatile release after 24 hours of a two component polyurethane

FIGURE 22

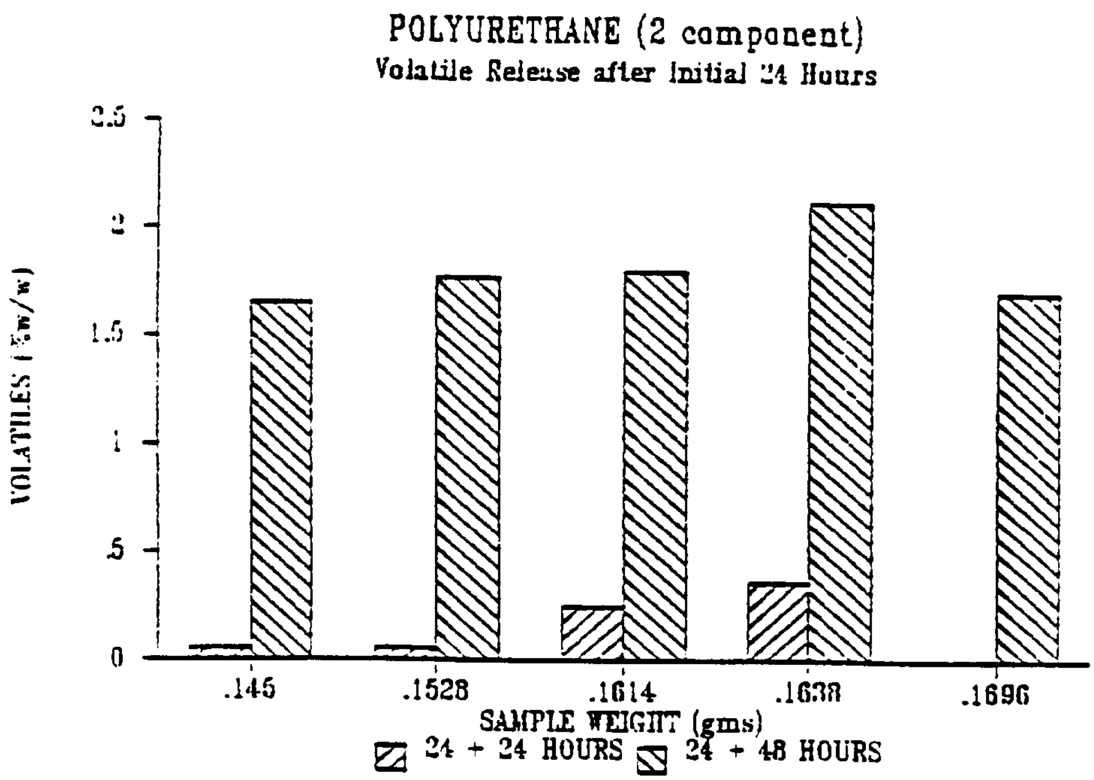


Figure 23. Volatile content of a single component urethane as a function of induction time

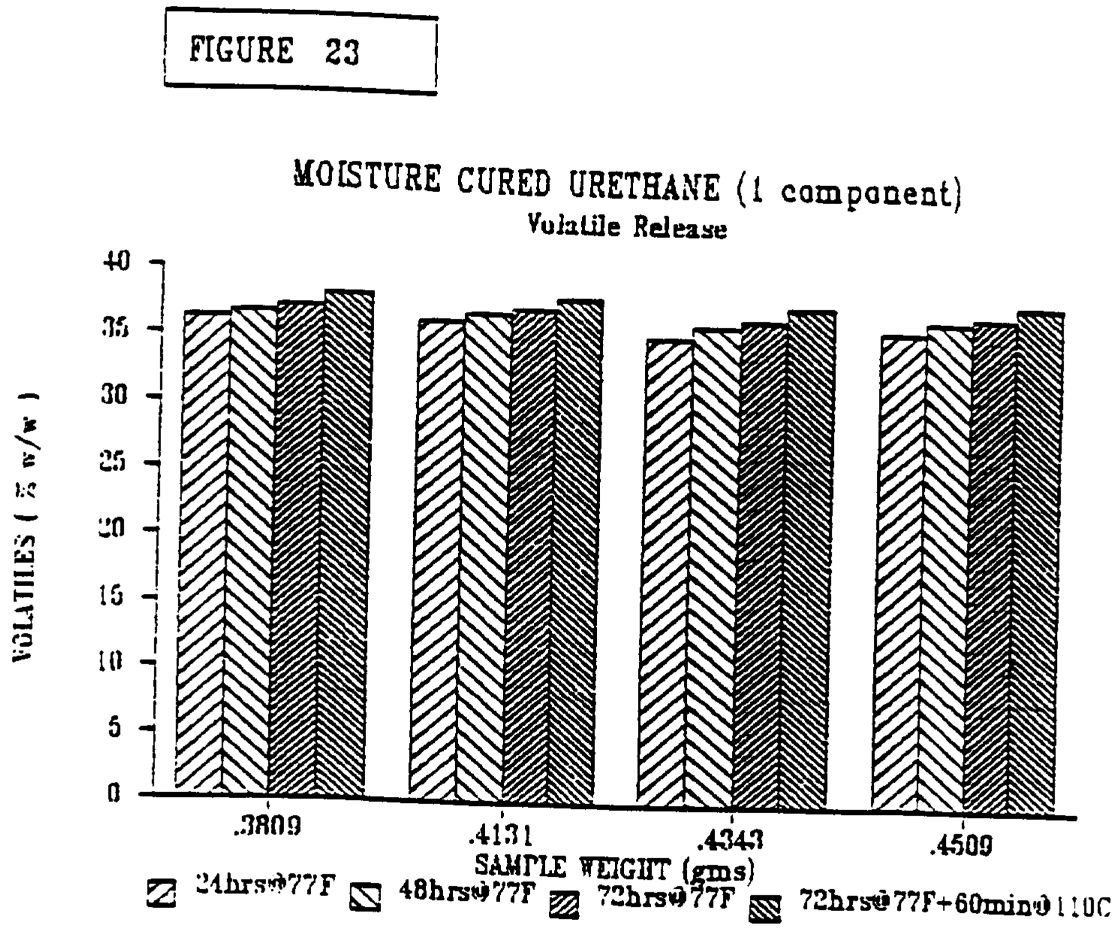


Figure 24. Volatile content of a single component urethane as a function of induction time

FIGURE 24

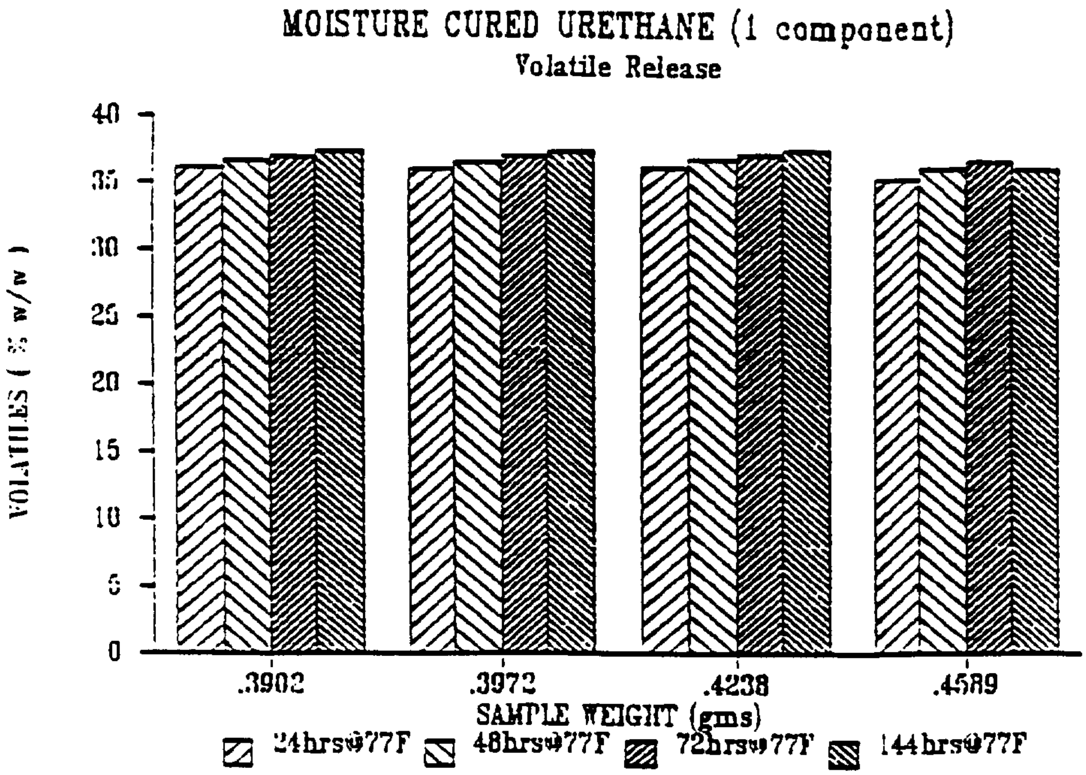


Table 23. Determination of a Volatile Content of a single component solvent-based acrylic enamel using different sample weights

Sample Weight grams	24 hour Cure at 77°F	24 hour cure at 77°F + 110°C for 60 minutes
0.1200	58.13	60.20
0.1891	58.33	60.60
0.2926	57.83	60.18
0.5267	57.74	60.22
0.6812	57.40	59.85
0.6917	57.38	59.88
0.6965	57.63	59.99
0.8840	57.05	59.58
1.0630	56.90	59.44
1.3308	56.24	59.01

Table 24. Volatile Content of a Solvent-Based 2-Component Polyurethane Using Manufacturer's Recommended Spreading Rate versus Long-term Ambient Cure

			Volatile Content* % (w/w)		
		(grams)	A	B	C
1.	No Induction Time	0.1450	47.80	47.86	49.45
		0.1528	48.43	48.47	50.20
		0.1614	46.28	46.53	48.08
		0.1638	46.04	46.40	48.17
		0.1696	47.88	47.70	49.59
2.	One hour Induction	0.1676	40.04	40.21	42.30
		0.5082	39.32	39.71	42.44
3.	Two hour Induction	0.1699	37.20	37.37	40.00
		0.5096	34.75	35.28	38.34

* Manufacturer's Recommended Spreading Rate - 610ft^{2}gal

Cure Schedule:

A - 24 hours at 77°F
B - 48 hours at 77°F
C - 48 hours at 77°F + 60 minute at 110°C

Table 25. Volatile Content of a Solvent-Based Single-Component Moisture-Cured Urethane Using Manufacturer's Recommended Spreading Rate versus Long-term Ambient Cure

Sample Wt. (grams)	Volatile Content* % (w/w) A	B	C	D	E
0.3809	36.23	36.23	37.12	38.15	-
0.3902	36.11	36.70	37.06	-	37.39
0.3902	36.13	36.63	37.08	-	37.39
0.4131	36.19	36.82	37.21	38.05	-
0.4238	36.29	36.88	37.28	-	37.61
0.4343	35.23	36.15	36.61	37.65	-
0.4580	35.48	36.64	37.10	38.05	-

* Manufacturer's Recommended Spreading Rate - 238ft^2/gal

Cure Schedule:

A - 24 hours at 77°F

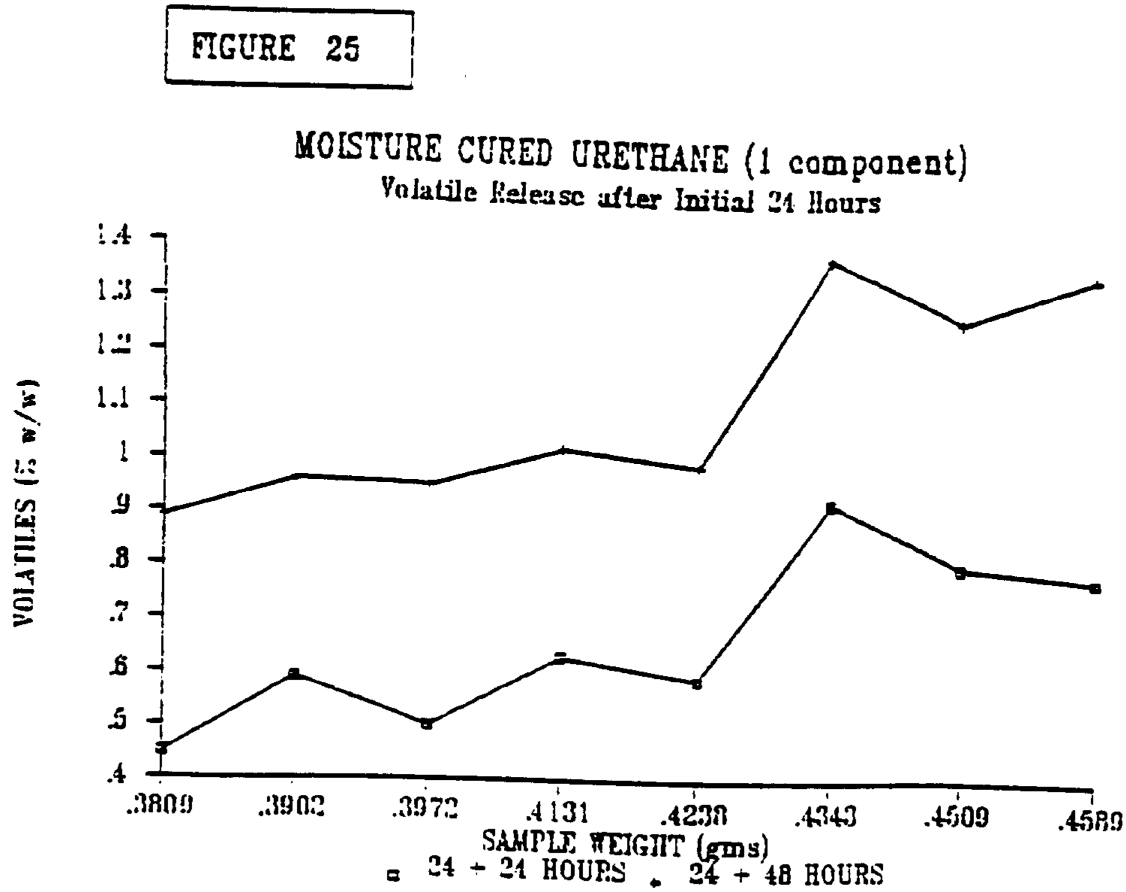
B - 48 hours at 77°F

C - 48 hours at 77°F

D - 72 hours at 77°F + 110°C for sixty (60) minutes

E - 144 hours at 77°F

Figure 25. Volatile content of a single component urethane as a function of sample size



L. Determination of the Total Volatiles emitted from a Single Component, Solvent-Based Traffic Paint Containing Exempt (1, 1, 1 Trichloroethane) solvent Varying Sample Weights using a 48 Hour Ambient Cure Using no Diluent.

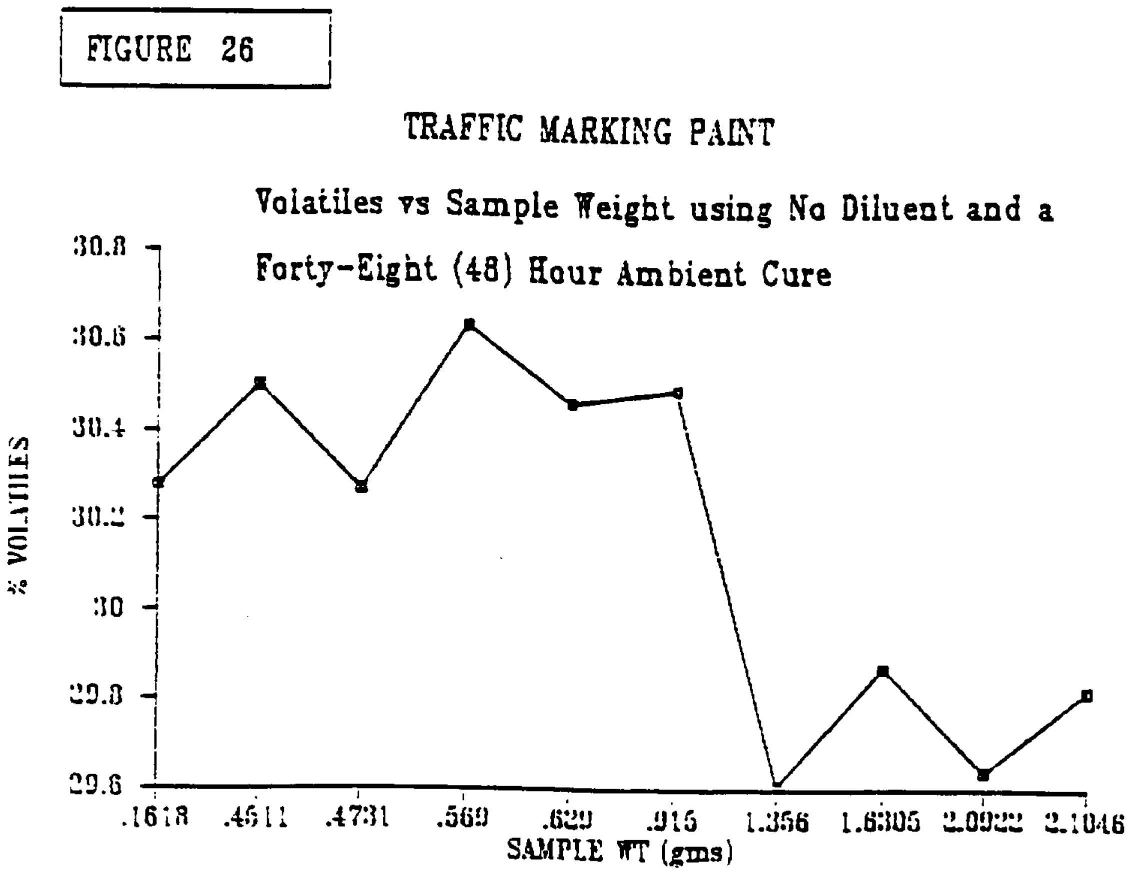
1. Summary of Test Method:

The coating sample size of the solvent-based traffic marking paint varied from 0.16g to 2.1g using no diluent. The total volatile content using the different sample weights was measured after an ambient cure time of forty-eight (48) hours.

2. Discussion:

Overall, the lowest sample weight gave the highest volatile content of 30.28% (w.w) and the highest sample weight gave the lowest volatile content of 29.82% (w/w). These numbers are given in **TABLE 26. Determination of Volatile Content of a Single component, Solvent-based Traffic Paint Using no Diluent and Varying Sample Weights at a Forty-eight (48) hour Ambient Cure** and displayed graphically in Figure 26.

Figure 26. Volatile content of a traffic marking paint as a function of sample size



M. Determination of the Total Volatiles emitted from a Single Component, Solvent-Based Wood Stain varying Sample Weights using a 48-hour Ambient Cure with 3 ml of a Toluene Diluent.

1. Summary of Test Method

The coating sample size of the Solvent-Based Wood Stain varied from 0.11g to 1.23g using three (3) mls of a toluene diluent. The Total Volatile Content using the different sample weights were measured after an Ambient Cure time of forty-eight (48) hours.

2. Discussion:

Overall, the lowest sample weight gave the highest volatile content of 79.43% (w/w) and the highest sample weight gave the lowest volatile content of 78.03% (w/w). These numbers are given in **TABLE 27. Determination of volatile Content of a Single Component, Solvent-based Wood Stain Using Three (3) mls of a Toluene Diluent varying Sample weights over a Forty-eight (48) hour Ambient Cure** and displayed graphically in Figure 27.

N. Determination of the Total volatiles emitted from a Single Component, Water-Based Steel Coating Varying Sample Weights using a 48-Hour Ambient Cure with three 3 ml of a Water Diluent.

1. Summary of Test Method

The coating sample size of the water-based steel coating varied from 0.13g to 1.27g using three (3) mls of the water diluent. The total volatile content using the different samples weights were measured after an ambient cure time of forty-eight (48) hours.

2. Discussion:

Overall, the lowest sample weight gave the highest volatile content of 59.86% (w/w) and the highest sample weight gave the lowest volatile content 58.73% (w/w). These numbers are given in **TABLE 28. Determination of Volatile Content of a Single Component, Water-based Coating for Steel Using three (3) mls of a Water Diluent Varying Sample Weights over a Forty-eight (48) Hour Ambient Cure** and displayed graphically in Figure 28.

Figure 27. Volatile content of a wood stain as a function of sample weight

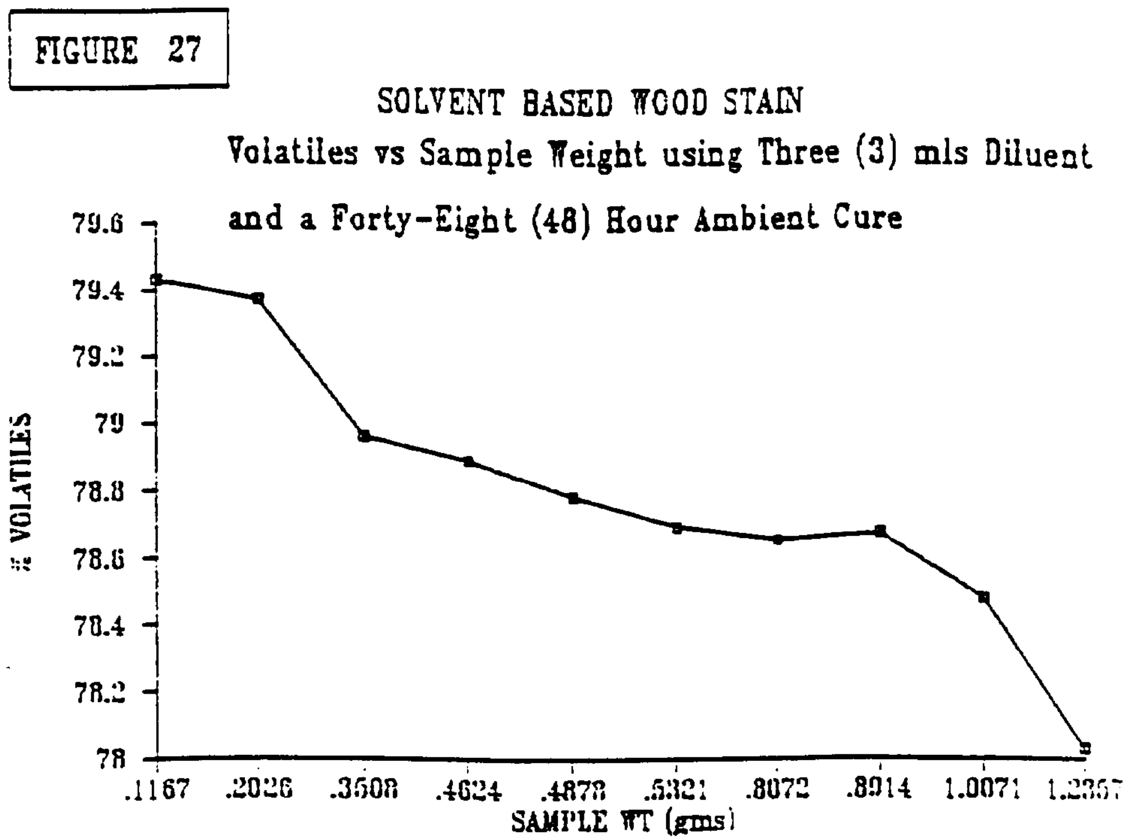


Table 26. Volatile Content of a Single Component Solvent-Based Traffic Paint Using No Diluent and Varying Sample Weights at a 48 Hour Ambient Cure

Coating Weight (g)	Total Volatile Content % (w/w)
1. 0.1618	30.28
2. 0.4511	30.50
3. 0.4731	30.27
4. 0.5690	30.63
5. 0.6290	30.46
6. 0.9150	30.49
7. 1.3560	29.61
8. 1.6303	29.87
9. 2.0922	29.64
10. 2.1046	29.82

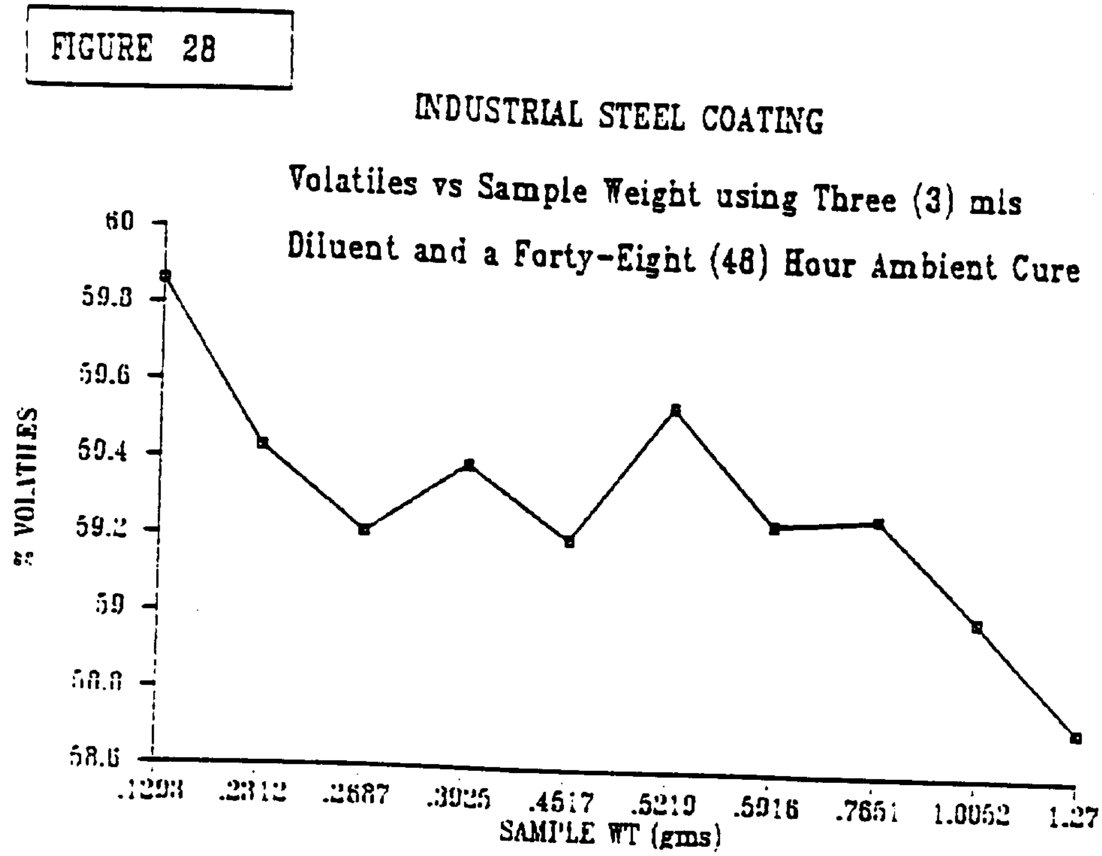
Table 27. Volatile Content of a Single Component Solvent-Based Wood Stain Using 3 ml of Toluene Diluent Varying Sample Weights Over a 48 Hour Ambient Cure

Coating Weight (g)	Total Volatile Content % (w/w)
1. 0.1167	79.43
2. 0.2026	79.37
3. 0.3506	78.96
4. 0.4624	78.89
5. 0.4878	78.78
6. 0.5321	78.69
7. 0.8072	78.65
8. 0.8914	78.67
9. 1.0071	78.43
10. 1.2357	78.03

Table 28. Determination of Volatile Content of a Single Component, Water-Based Coating For Steel Using 3 mls of Water as a Diluent Varying Sample Weights Over a 48 Hour Ambient Cure

	Coating Weight (g)	Total Volatile Content % (w/w)
1.	0.1293	59.86
2.	0.2312	59.43
3.	0.2687	59.21
4.	0.3925	59.39
5.	0.4517	59.20
6.	0.5219	59.55
7.	0.5916	59.25
8.	0.7651	59.27
9.	1.0052	59.01
10.	1.2700	58.73

Figure 28. Volatile content of an industrial steel coating as a function of sample weight



O. Determination of Volatile Organic Compound (VOC) Content of a Single Component, Solvent-Based Coating versus Volatile Content as a Function of Coating Density.

1. Summary of Test Method

The theoretical VOC of a single component, solvent-based coating was calculated using varying volatile contents and densities. The equation used for the calculation was VOC (g/liter) = (100-N) (D) 10 where N = Total non-volatile (NV) content and D = density of coating in g/mls.

2. Discussion

The coating sample with the highest solids (NV) and lowest density yields the lowest VOC. Consequently, the coating with the lowest solids (NV) and highest density yields the highest VOC.

Table 29. Volatile Organic Content vs Volatile Content as a Function of Coating Density

Volatile Content (% w/w)	Coating Density (g/ml) 0.5	1.0	1.5	2.0	2.5
100	500	1000	1500	2000	2500
90	450	900	1350	1800	2250
80	400	800	1200	1600	2000
70	350	700	1050	1400	1750
60	300	600	900	1200	1500
50	250	500	750	1000	1200
40	200	400	600	800	1000
30	150	300	450	600	750
20	100	200	300	400	500
10	50	100	150	200	250
0	0	0	0	0	0

[1] Coating used was a single component solvent-based sample containing no exempt solvents where VOC was calculated using the following equation.

*VOC = (100 - N) (D) (10) where
N = Total Non-volatile (wt. percent)
D = Density of coating in g/ml

7. DCM and TCA BY PROPOSED GC -- Summary of Results Using Proposed Method for Determination of Dichloromethane and 1,1,1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph (ASTM D4457)

Calcoast Labs conducted an intralaboratory survey using the proposed modifications to ASTM D4457 to determine the effectiveness of those proposed modifications on reproducibility, precision, and accuracy of the test method.

The intralaboratory survey included using different operators on different days analyzing the same samples using the modified ASTM D4457 and the original ASTM D4457 specification.

A. Types of Coatings Analyzed

The dichloromethane and 1,1,1 Trichloroethane was measured for a total of 22 samples of 6 types of coatings, using the proposed modifications to ASTM D4457. The coatings analyzed included:

1. Air Dry Alkyd Enamel
2. Baked Alkyd Enamel
3. Alkyd Enamel
4. Two-Component Polyurethane
5. Oil-Based Wood Preservative
6. Hi-Solids Two-Component Polyamide Epoxy

Total Coatings Analyzed: 22

The coating samples analyzed contained low, medium, and high concentrations of 1,1,1 trichloroethane and methylene chloride solvents.

B. Proposed modifications to ASTM D4457

Proposed modifications to ASTM D4457 - determination of dichloromethane and 1,1,1 trichloroethane in paints and coatings by direct injection into a gas chromatograph

Parameter	ASTM D4457	Proposed Modification
a. Detector		
1. Type	Thermal Conductivity or Flame Ionization Detector (FID)	FID required
2. Temperature	250° C	240° C
b. Injector Temperature	200° C	240° C
c. Carrier Gas Flow Rate mls/min.	30	30
d. Column		
1. Type	Porous Polymer	10% sp-2100
2. Length	4' x 1/8"	20' x 1/8"
3/ mesh	80/100	80/100
e. Column Temperature ° C		
1. Initial	100	55 (3 min.)
2. Final	230 (8 min.)	185 (15 min.)
3. Program Rate	8 °C/min	6 °C/min
f. Sample Preparation		
1. Size	5.0g	1.2g
2. Internal Standard	1-propanol(2g)	Tetrahydrofuran THF (0.5g)
3. Diluent	DMF (16g)	Propyleneglycol methylether PGME (5g)
4. Sample/ Diluent Ratio	0.31:1	0.24:1
5. Centrifuge Time & Speed:	5 minutes @ 1000 rpm	20 minutes @ 5000 rpm

C. Reasons For the Proposed Modifications to ASTM D4457

1. Tetrahydrofuran (THF) is used as the internal standard bercause it is much more compatible with solvent-based systems than 1-propanol.

2. Propylene glycol methyl ether (PGME) is used in place of DMF because it is also much more compatible with solvents and resins likely to be used in solvent-based coatings. It also allows much cleaner separation between pigment and resin solids/solvents.

3. A flame ionization detector (FID) is recommended over a thermal conductivity detector (TCD) due to its greater sensitivity.

4. A sintered glass liner is recommended over a pre-column packed with glass wool because it allows a more uniform heated evaporation zone, reduces dead space, and prevents sludge buildup in the column entrance.

5. A non-polar SP-2100, 20 foot column is recommended because it allows greater separation of the hydrocarbon solvents likely to be present than does the specified porous polymer column.

6. An initial column temperature of 55°C for 3 minutes (using the SP-2100) is recommended to allow for detection of very light chlorinated hydrocarbon solvents which may be present.

7. An increase in sample-to-diluent ratio is used to increase the detection limits for possible chlorinated hydrocarbons present.

8. Centrifugation at 5000 RPM for 20 minutes instead of 1000 RPM for 5 minutes allows a much cleaner separation between pigment and resins solids/solvents and minimizes sludge buildup in the injector port.

9. Intralaboratory surveys using the above procedures for solvent-based coatings including alkyds and multiple-component systems, such as polyurethanes and epoxies have given reproducibility (relative percent) numbers of 1.5 for methlyene chloride and 1.1 for trichloroethane.

8. PROPOSED vs. EXISTING GC -- Comparison of Test Methods for Determination of Dichloromethane and 1, 1, 1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph (ASTM D4457)

Discussion:

A. Analysis Parameter

The reproducibilty (relative %) numbers obtained for both modified and unmodified versions of ASTM D4457 reflect an average of eight (8) separate analyses performed. Coating samples with low, medium, and high concentrations of 1,1,1 trichloroethane and methylene chloride were used.

B. Modified Test Procedure, Methylene Chloride

Different operators on different days using the modified ASTM D4457 specification obtained reproducibilty (relative %) numbers with low, medium, and high concentrations of methylene chloride of **1.1, 0.7,** and **0.7,** respectively. These numbers are given in **TABLE 30.** and are displayed graphically in **FIGURES 29** and **30.**

C. Existing Test Procedure, Methylene Chloride

Different operators on different days using the unmodified (original) ASTM D4457 specification obtained reproducibilty (relative %) numbers with low, medium, and high concentrations of methylene chloride of **16.4, 19.0,** and **14.5,** respectively. These numbers are given in bold type in **TABLE 30** and displayed graphically in **FIGURES 29** and **30.** While the coating sample with medium DCM content had a relative reproducibilty of 19.0 %, the coating samples with low and high DCM concentrations are in agreement with the QA/QC criteria of a relative reproducibility of **17.92 %** as stated in the original ASTM D4457 specification.

The actual DCM content obtained using the modified ASTM D4457 procedure deviated only slightly (<1%) from the theoretical values. The actual DCM content obtained using the unmodified procedure varied greatly (between 7 to 18 %) from the theoretical values. These values are displayed graphically in **FIGURE 31.**

D. Modified Test Procedure, 1,1,1 TCA

Different operators on different days using the modified ASTM D4457 specification obtained relative reproducibility (%) numbers with low, medium, and high concentrations of 1,1,1 TCA of **1.4**, **1.1**, and **0.1**, respectively. These numbers are given in bold type in **TABLE 31** and displayed graphically in **FIGURES 32** and **33**.

E. Existing Test Procedure, 1,1,1 TCA

Different operators on different days using the unmodified (original) ASTM D4457 specification obtained relative reproducibility (%) numbers with low, medium, and high concentrations of 1,1,1 TCA of **8.0**, **10.4**, and **6.0**, respectively. These numbers are given in bold type in **TABLE 31.** While the coating sample with medium TCA content had relative reproducibility (%) of **10.4**, the coating samples with low and high TCA concentrations are within the QC/QA criteria of relative reproducibility (%) of **8.1** as stated in the original ASTM D4457 specification.

The actual 1,1,1 TCA content obtained using the modified procedure deviated only slightly (<1%) from the theoretical values. The actual 1,1,1 TCA content obtained using the unmodified procedure varied greatly (between 1 and 14%) from the theoretical values. These numbers are displayed in **FIGURE 34**.

F. Summary of Modified DCM and TCA Content

Summary of Dichloromethane(DCM) and 1,1,1 Trichloroethane (TCA) Content of Solvent-Based Coatings Analyzed by Gas Chromatography -- Modified ASTM D4457

	Cl-HC %(w/w)		RPD			Percent Recovery		
Coating Type	DCM	TCA	DCM	TCA	Diluent	DCM	SL*	TCA
a. Air Dry Alkyd Enamel	4.83	1.52	0.31	0.40	Propylene Glycol Methyl Ether (PGME)	93		94
b. Baked Alkyd Enamel	1.80	1.57	0.11	0.31	PGME	100		96
c. Alkyd Enamel	4.30	4.20	0.45	0.40	PGME	89	10%	101
						100	40%	97
						94	70%	96
d. Two (2) Component Polyurethane	1.74	3.85	0.51	0.48	PGME	100	10%	101
						103	40%	103
						95	70%	98
e. Oil-Based Wood Preservative	3.21	5.49	0.38	0.20	PGME	101	10%	98
f. Hi-Solids Two(2) Component Polyamide Epoxy	4.45	5.93	0.41	0.28	PGME	98	10%	97

Total Coatings Analyzed: 22

*SL = Spike Level

Table 30. Dichloromethane Content of Coatings, Using Modified and Unmodified ASTM D4457

Coating	Day 1 OP1	Day 1 OP2	Day 2 OP1	Day 2 OP2	Theoretical	RPD	Reproducibility* (Relative %)
	Dichloromethane (DCM) Content[1] (% w/w)						
A. Modified[2]							
1. Oil-based Alkyd(low DCM)	13.45	13.81	13.21	13.90	13.77	1.64	1.1
2. Oil-based Alkyd(mid DCM)	24.89	25.49	25.09	25.21	25.13	0.80	0.7
3. Oil-based Alkyd (high DCM)	32.71	33.20	32.80	33.01	33.05	0.27	0.7
B. Unmodified[3]							
4. Oil-based Alkyd(low DCM)	3.03	4.15	2.98	4.21	11.38	1.34	16.4
5. Oil-based Alkyd(mid DCM)	2.95	4.64	3.01	4.13	16.83	2.01	19.0
6. Oil-based Alkyd (high DCM)	11.56	8.34	11.45	8.82	27.78	2.80	14.5

* Between operators

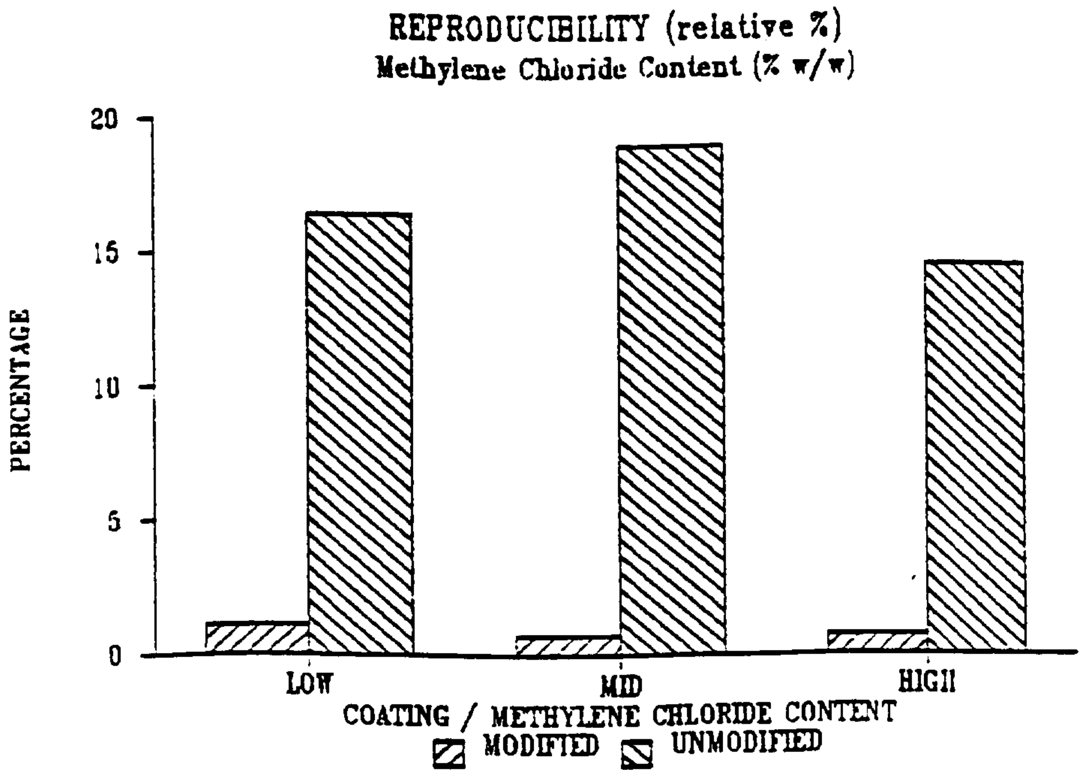
[1] DCM results given are an average of duplicates obtained by each operator on a given day.

[2] Modifications to ASTM D4457-"Determination of Dichloromethane and 1,1,1 Trichloroethane in Paints and Coatings by Direct Injection Into a Gas Chromatograph" used to achieve these results are given in **Proposed Modifications to ASTM D4457**.

[3] Unmodified refers to using the original ASTM D4457 specification as printed.

Figure 29. Intralaboratory relative reproducibility using modified and unmodified ASTM D4457 (DCM)

FIGURE 29 INTRALABORATORY RELATIVE REPRODUCIBILITY



THE SAME COATINGS WERE ANALYZED USING MODIFIED AND UNMODIFIED ASTM D4457

Figure 30. Intralaboratory relative reproducibility using modified and unmodified ASTM D4457 (DCM)

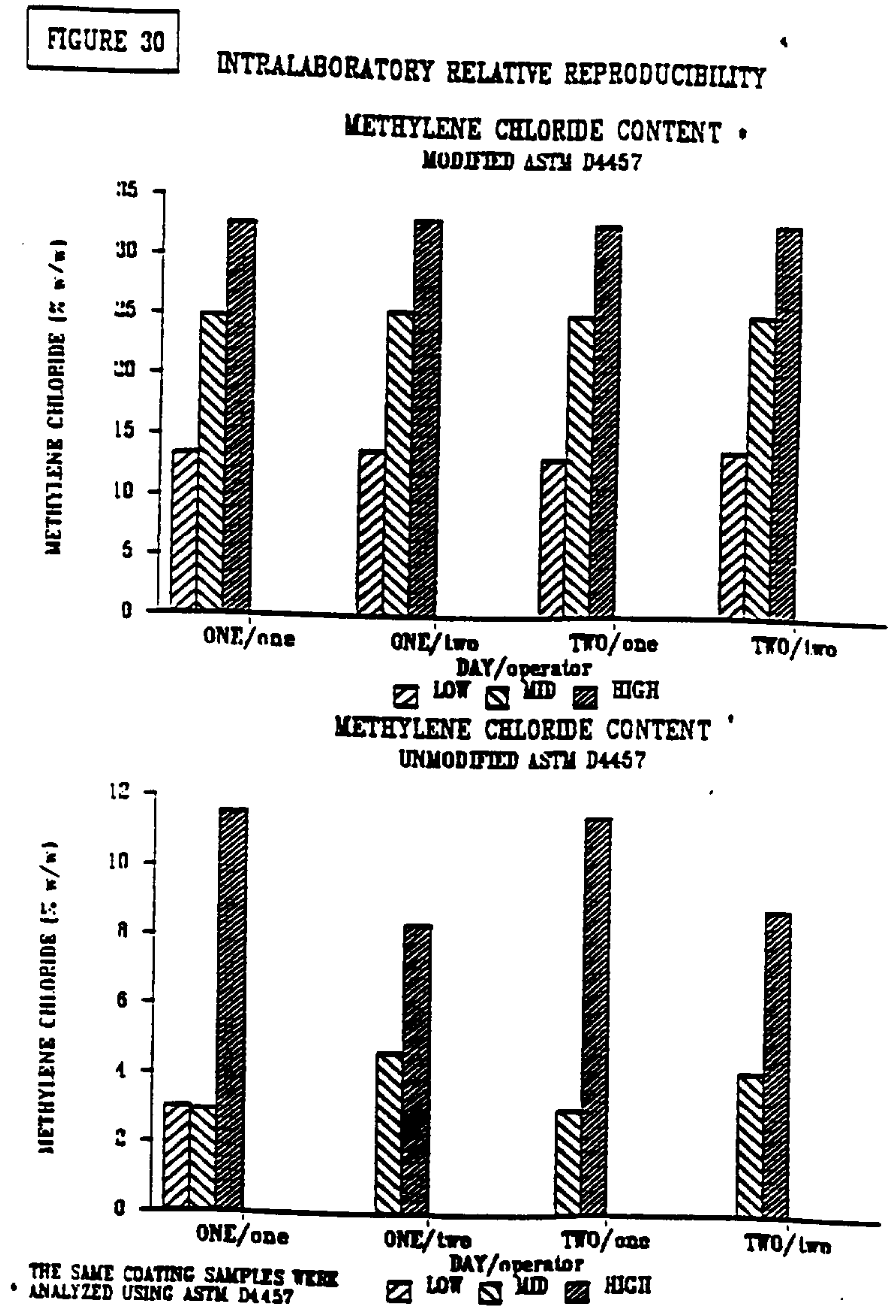


Figure 31. Error comparison of modified and unmodified ASTM D4457 (DCM)

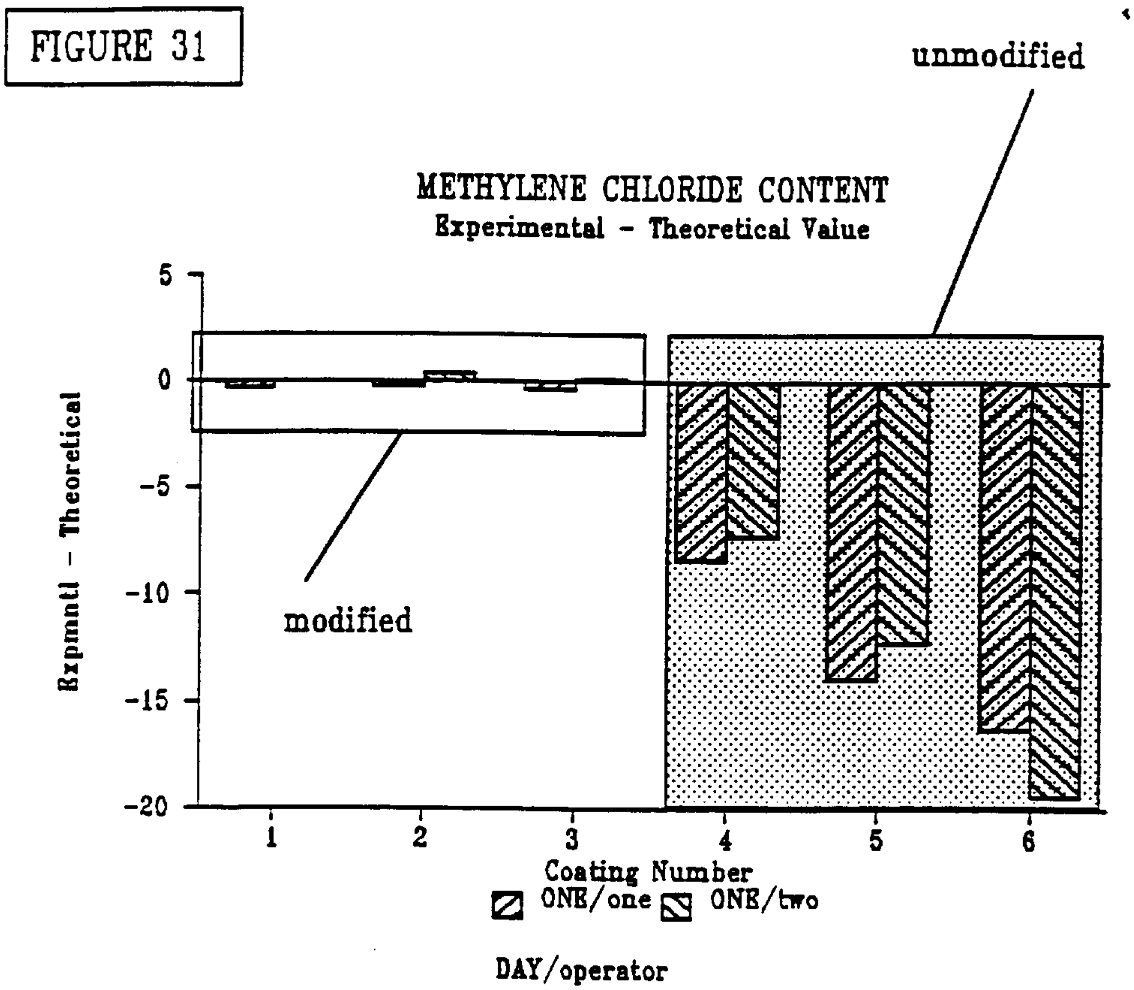


Table 31. 1,1,1 Trichloroethane Content of Coatings, Using Modified and Unmodified ASTM D4457

1,1,1 Trichloroethane(TCA) Content[5]

Coating	Day 1 OP1	Day 1 OP2	Day 2 OP1	Day 2 OP2	Theoretical	RPD	Reproducibility* (Relative%)[4]
A. Modified[2]							
1. Oil-based Alkyd (low TCA)	13.91	13.41	13.83	13.55	13.45	0.58	1.4
2. Oil-based Alkyd (mid TCA)	20.95	20.32	20.71	20.45	20.12	0.58	1.1
3. Oil-based Alkyd (high TCA)	27.01	26.94	26.89	26.89	26.84	0.22	0.1
B. Unmodified[3]							
4. Oil-based Alkyd (low TCA)	34.40	28.76	33.20	29.02	20.01	3.55	8.0
5. Oil-based Alkyd (mid TCA)	32.68	29.11	33.09	28.43	24.42	1.25	10.4
6. Oil-based Alkyd (high TCA)	26.77	30.05	27.84	31.62	27.78	1.98	6.0

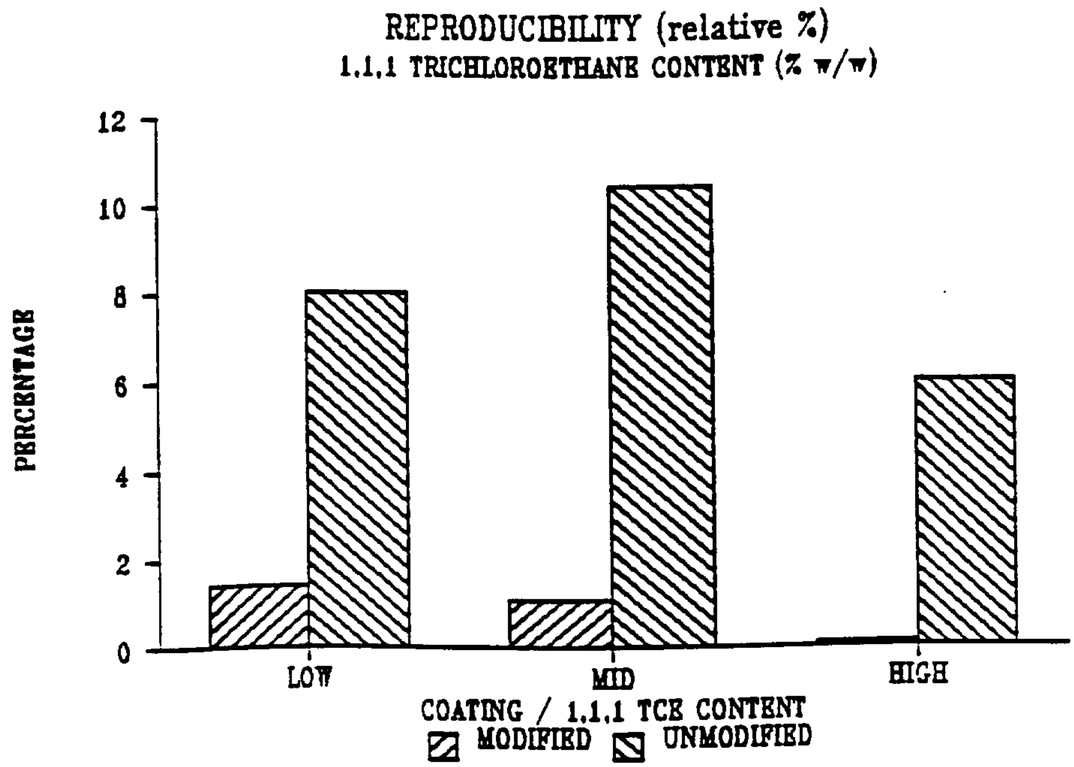
* Between operators

[4] Reproducibility between operators (Relative %) results are calculated as an average between two(2) results obtained by two(2) different operators on two(2) different days.

[5] TCA Content results given are an average of duplicates obtained by each operator on a given day.

Figure 32. Intralaboratory relative reproducibility using modified and unmodified ASTM D4457 (TCA)

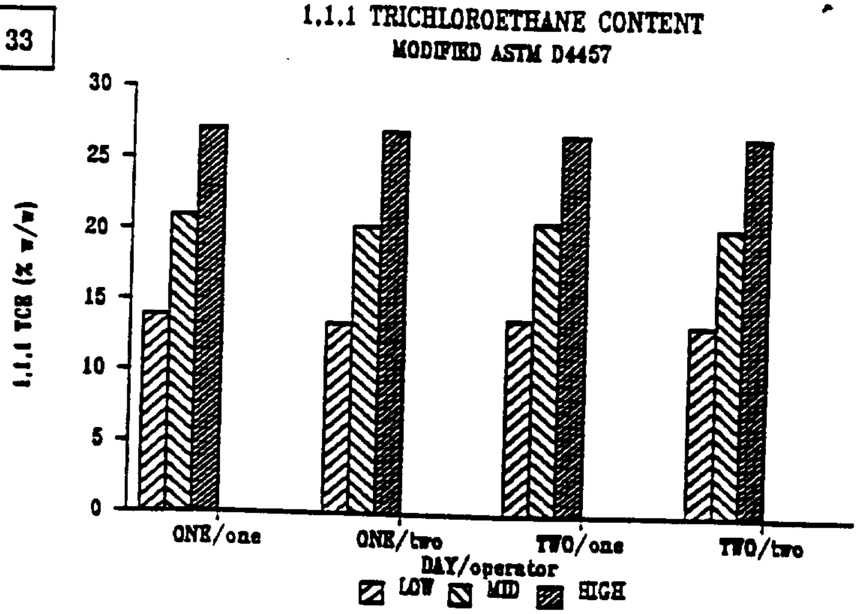
FIGURE 32 INTRALABORATORY RELATIVE REPRODUCIBILITY-ASTM D4457

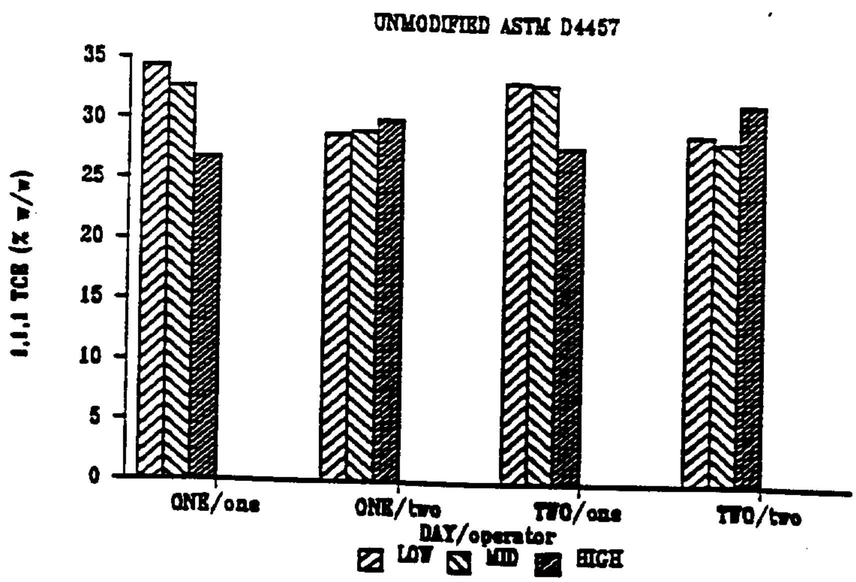


THE SAME COATING SAMPLES WERE ANALYZED USING MODIFIED AND UNMODIFIED ASTM D4457

Figure 33. Intralaboratory relative reproducibility using modified and unmodified ASTM D4457 (TCA)

FIGURE 33

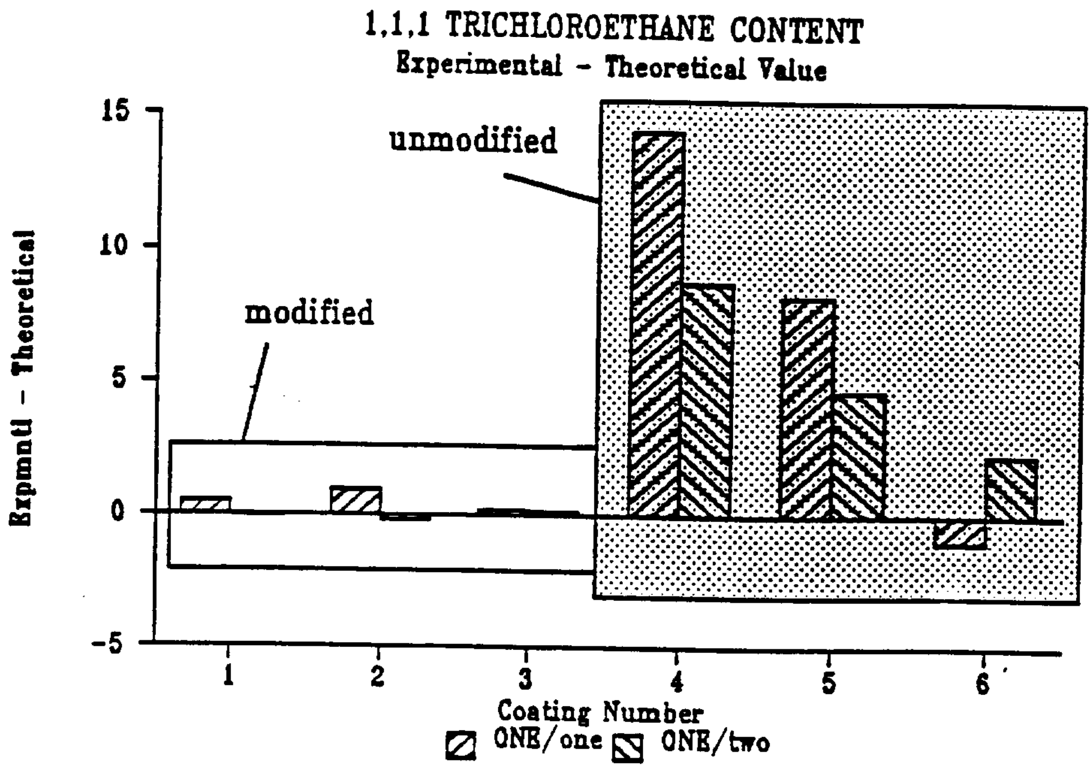




THE SAME COATING SAMPLES WERE ANALYZED USING MODIFIED AND UNMODIFIED ASTM D4457

Figure 34. Absolute error comparison of modified and unmodified ASTM D4457 (TCA)

FIGURE 34



THE SAME COATING SAMPLES WERE ANALYZED USING MODIFIED AND UNMODIFIED ASTM D4457

9. DENSITY BY EXISTING METHOD -- Discussion of Existing Test Method for Density of Paint, Varnish, and Related Products (ASTM D1475)

The relative percent reproducibility of the existing test specification is 1.5. Test methods which may yield a lower relative percent reproduciblity such as the use of a gas pycnometer are available.

The level of operator expertise required for using the equipment required for using the existing ASTM D1475 is relatively low. The cost of the equipment needed to perform that testing specification is also relatively low.

Measuring the density of certain types of coatings using the existing ASTM D1475 specification does present some problems. These types of coatings include gels* and powder coatings. Whether the density is measured loose or packed has great effect on the observed density.

It is the opinion of Calcoast Analytical Labs that the existing ASTM D1475 testing specification as written is sufficient for measuring the density of most coatings and need not be modified. At present, a cheaper, easier, more accurate method for measuring the densities of coatings is not available.

10. EXPERIMENTAL VOC -- Summary of Results Using Experimental and Theoretical Methods for Determination of Volatile Organic Compound Content of Paints and Related Coatings (ASTM D3960)

Determination of Volatile Organic Compound(VOC) Content of a Single Component, Solvent-Based Coating Versus Volatile Content as a Function of Coating density.

Summary of Test Method

The theoretical Volatile Organic Content (VOC) of a single component, solvent-based coating was calculated using varying volatile contents and densities. the equation used for the calculation was VOC (g/liter) = (100-N) (D) 10 where N = total non-volatile(NV) content and D = density of coating in g/ml.

Discussion

The coating sample with the highest solids (NV) and lowest density yields the lowest VOC. Consequently, the coating with the lowest solids (NV) and highest density yields the highest VOC.

Table 32. Volatile Organic Content vs Volatile Content as a Function of Coating Density

Volatile Content (% w/w)	Coating Density (g/ml)				
	0.5	1.0	1.5	2.0	2.5
	VOC (g/Liter)				
100	500	1000	1500	2000	2500
90	450	900	1350	1800	2250
80	400	800	1200	1600	2000
70	350	700	1050	1400	1750
60	300	600	900	1200	1500
50	250	500	750	1000	1250
40	200	400	600	800	1000
30	150	300	450	600	750
20	100	200	300	400	500
10	50	100	150	200	250
0	0	0	0	0	0

A. Determination of Volatile Organic Compound (VOC) Content of Three Single Component Water-Based Inks as a function of Temperature Used for the Determination of Total Volatile Content.

1. Summary of Test Method

The VOC content was determined for three (3) water-based ink samples using two (2) different temperatures and heating times for determination of total volatile content. The temperatures/heating time used included:

1. Conventional ASTM D2369 (110°C for sixty (60) minutes)
2. 120°F for seventy-five (75) minutes.

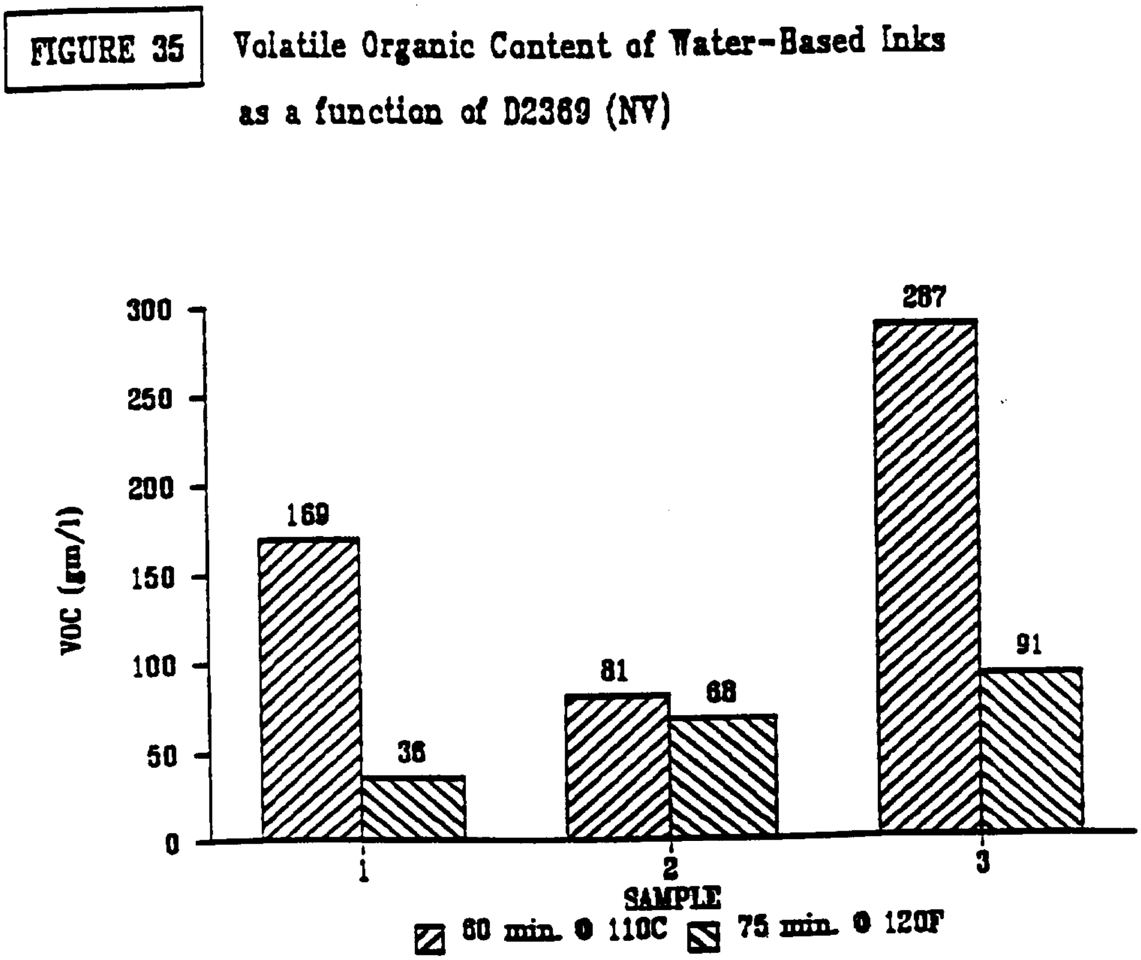
The water content of the ink samples was analyzed by KF titration and direct injection gas chromatography (GC). The coating densities were measured and corresponding VOCs determined using the minus water calculation incorporated in ASTM D3960.

2. Discussion

Water-based ink sample 3 contained the highest VOC content of 287 g/liter measured at110°C for sixty (60) minutes. The VOCs for samples 1 and 2 were 169 and 81 g/liter, respectively. The VOCs measured for the coating samples using 120°F for seventy-five(75) minutes were 36, 68, and 91 g/liter, respectively. All ink manufacturers considered their products to be "no" VOC inks. All ink manufacturers felt that the volatile content measured at 110°C for sixty(60) minutes is not representative of the total volatiles emitted during the actual application process in which drying time and temperature used were seventy-five(75) minutes and 120°F, respectively. This point is valid only if the volatile components which were driven off at 110°C will coreact and remain in the film at 120°F.

Otherwise, the organic components do have a vapor pressure and will eventually be emitted as VOC. These VOC numbers obtained are given in **TABLE 35** and displayed graphically in **FIGURE 35** on.

Figure 35. Volatile organic content (VOC) of water base inks as a function of NV (ASTM D2369)



B. Volatile Compound Identification by Gas Chromatography and the Effects of Temperature on the Measurement of the Volatile Organic Compounds when Determining the VOC Content of Three Single Component, Water-based Inks.

1. Summary of Test Method

The ink samples were placed in borosilicate head-space vials and sealed with an aluminum cap, teflon septum, star spring, and hand crimper. The vials were heated at 110°C for thirty (30) minutes, pressurized for four (4) minutes, and the vapor injected on-column for five(5) seconds. The GC detector used was an FID and the column was a non-polar, SP-2100. Standards consisting of various hydrocarbons, ketones, and alcohols were headspaced under the same GC operating parameters as the samples. The total volatile content (minus water) was then broken down into the various organic volatile compounds present.

Table 34. Volatile Organic Compound Identification by Headspace Gas Chromatography for Three Single-Component water-based Inks

	Volatile Composition of Ink Sample* % (w/w)		
Organic Component	1	2	3
A. Volatile monomeric alcohols - methanol,	17.64	77.94	23.37
b. Volatile Polyols and Diols - ethylene glycol	25.75	10.27	72.21
C. Semi-volatile polyols and diols-propylene glycol	56.61	11.79	4.42

*Organic Compounds are given as weight percent of total volatiles other than water detected.

2. Discussion

The headspace GC analysis of the volatile components of the coatings is consistent with both the VOC measured at 110°C and VOC measured at 120°F for seventy-five(75) minutes.

The ink sample which contained the highest measured VOC (minus water) in g/liter measured at 110°C for sixty (60) minutes contained the lowest amount of high boiling compounds such as polyols, diols, and propylene glycol. The VOC measured at 120°F for seventy -five (75) minutes for the same sample was also the highest.

The ink sample which had the lowest VOC measured at 110°C for sixty (60) minutes had the next to lowest VOC measured at 120°F for seventy-five(75) minutes due to its higher volatile monomeric alcohols(i.e. methanol, ethanol etc. content. These values are given in **TABLE 34** above.

C. The Effect of Using the Minus Water Calculation (VOC1 vs VOC2) on the Determination of Volatile Organic Compound (VOC) Content of Three Single Component, Water-Based Inks Formulated for Identical Usage.

1. Summary of Test Method

The volatile organic compounds (VOC) content of three (3) water-based inks was calculated using VOC1 and VOC2 (minus water) calculations incorporated into ASTM D3960. The percent increase in total VOC content was then calculated.

2. Discussion:

The VOC in g/liter using the VOC2 minus water calculation increased an average of 248 percent.

$$VOC1 = (\%\ volatile - \%\ water)\ (Dm)\ (10)$$

$$VOC2 = \frac{VOC1\ (100)}{(100 - \%\ WATER\ {*}Dm/Dw)}$$

Where: Dm = density of coating (g/ml)
Dw = density of water (g/ml)

These numbers are given in **TABLE 36. The effect of using the Minus Water Calculation (VOC1 vs VOC2) on the Determination of Volatile Organic Compound (VOC) Content of Three (3) Single Component Water based Inks Formulated for Identical Usage**

D. Determination of volatile Organic Compound (VOC) Content of a water-based Coating Varying Percent Volatiles versus Water Content Using the Minus Water (VOC2) Calculation.

1. Summary of Test Method

The theoretical VOC content of six (6) water-based coatings was formulated to be 500 g/liter using the VOC1 calculation and varying water content versus volatiles from 0% vs. 50% to 100% vs. 50%. The VOC2 (minus water calculations were then determined.

2. Discussion

When the volatile content is 50% and water content is 0% the VOC2 calculation yields a VOC of 500 g/liter.

When the volatile content is 60% and water content is 10%, the VOC2 calculation yields a VOC content of 550 g/liter. When the volatile content is 100% and water content is 50%, the VOC2 calculation yields a VOC of 1000 g/liter. These numbers are given in **TABLE 36 Determination of Volatile Organic Compound (VOC) Content of a Water-based Coating Varying Percent Volatiles versus Water Content Using the Minus Water Calculation (VOC2)** and displayed graphically in Figure 36.

E. Determination of Volatile Organic Compound (VOC) Content of a Water-based coating using VOC1 and VOC2 (minus water Calculations.

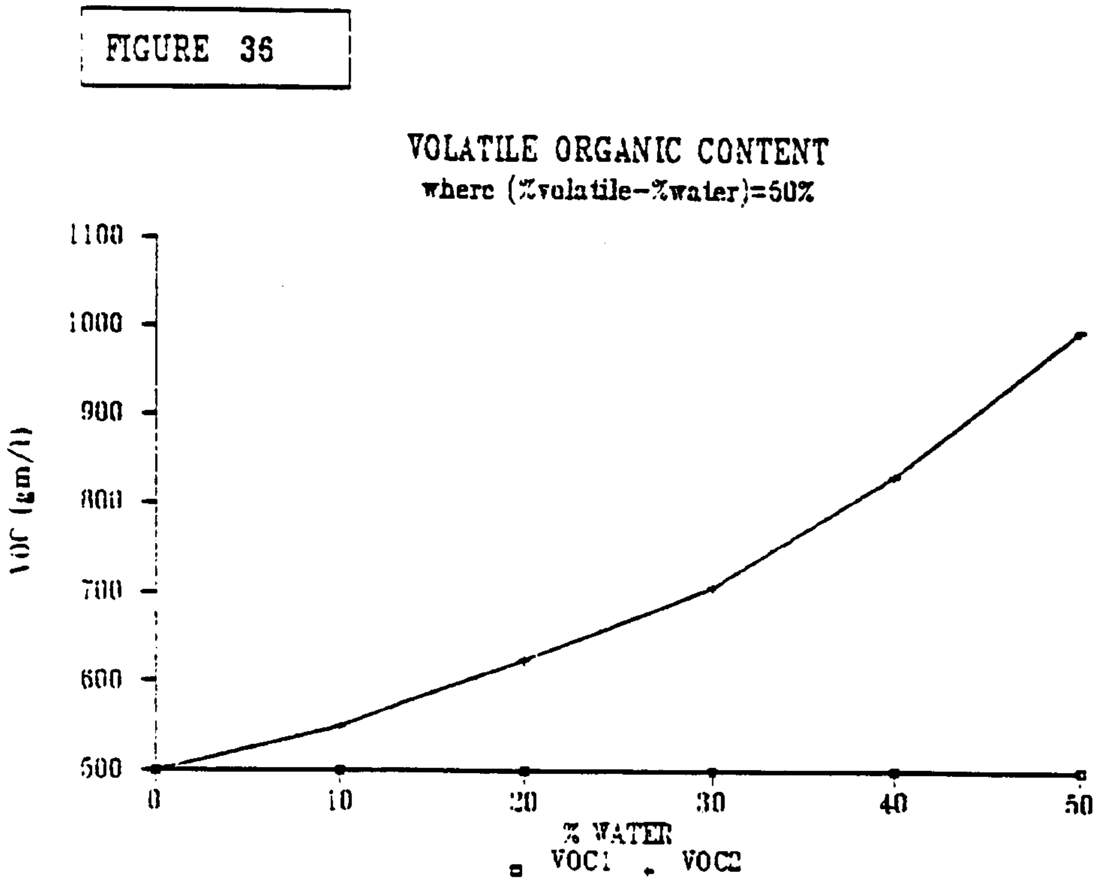
1. Summary of Test Method

The theoretical VOC1 and VOC2 were calculated for a water-based coating varying water content and percent volatiles. The relationship between water content, percent volatiles and the resulting VOC1 and VOC2 content were then expressed.

2. Discussion

The VOC1 calculation for VOC of a water-based coating containing 40% volatiles and 20% water is 200 g/liter. The VOC2 calculation for VOC of the same coating would be approximately 250 g/liter. These VOC1 and VOC2 numbers can be used as a guide in coating formulation to meet a desired VOC2 limit by knowing the water content and volatile content of a particular coating of interest. These numbers are given in **TABLE 37 Determination of Volatile Organic Compound (VOC) Content of a Water Based coating using VOC1 and VOC2 (minus water) Calculations** and displayed graphically in Figure 37.

Figure 36. Volatile organic content (VOC) of a 50% volatile coating as a function of water content



F. Determination of Volatile Organic Compound (VOC) Content of a Solvent-based Coating Containing Chlorinated (Exempt) Solvents using VOC1 and VOC2 (minus exempt solvent).

Calculations

1. Summary of Test Method

The theoretical VOC1 and VOC2 were calculated for a solvent-based coating varying exempt solvent content and percent volatiles. The relationship between exempt solvent content, percent volatiles and the resulting VOC1 and VOC2 content were then expressed.

2. Discussion

The VOC1 calculation for VOC of a solvent-based coating containing 40% volatiles and 10% exempt solvents is 200 g/liter. The VOC2 calculation for VOC of the same coating would approximately be 250 g/liter. These VOC1 and VOC2 numbers can be used as a guide in coating formulation to meet a desired VOC2 limit by knowing the exempt solvent content and volatile content of a particular coating of interest. These numbers are given in **TABLE 38, Determination of Volatile Organic Compound (VOC) Content of a Solvent-Based Coating Containing Chlorinated (Exempt) Solvents Using VOC1 and VOC2 (minus exempt solvent) Calculations** and displayed graphically in Figure 38.

Table 33. Volatile Organic Content of three Single Component Water-Based Inks as a Function of the Temperature Used for Determination of Total Volatile Content

	Volatile Organic Compound (VOC) Content* (g/liter)	
Sample	60 min at 110°C	75 min at 120°F
1	169	36
2	81	68
3	287	91

*VOC was calculated using VOC (minus water) calculation

Table 35. The Effect of Using the Minus Water Calculation (VOC1 vs VOC2) on the Determination of VOC for Three Single-Component Water-Based Inks Formulated for Identical Usage

	Volatile Organic Compound (VOC) Content - g/liter		
Ink Sample	VOC1	VOC2	Percent VOC Increase
1	76	169	222
2	34	81	238
3	101	287	284

Table 36. Effect of Water Content on VOC2 of a Water-Based Coating with a Constant Total Organic Volatile (VOC1)

Determination of Volatile Organic compound (VOC) Content of a Water-based Coating Varying Percent Volatiles versus Water Content using the Minus water Calculation (VOC2)

Parameters where:
VOC1 = 500 g/liter

	% Volatile	% H_2O	Resulting VOC2 (minus Minus Water)
1.	50	0	500
2.	60	10	550
3.	70	20	625
4.	80	30	708
5.	90	40	833
6.	100	50	1000

Table 37. Volatile Organic Content (VOC) of a Water-Based Coating

Determination of Volatile Organic compound (VOC) Content of a Water-based Coating Using VOC1 and VOC2 (minus water) Calculations

% Volatile	% water										
	0	10	20	30	40	50	60	70	80	90	100
					VOC1 (g/liter)*						
0	0	-	-	-	-	-	-	-	-	-	-
10	100	0	-	-	-	-	-	-	-	-	-
20	200	100	0	-	-	-	-	-	-	-	-
30	300	200	100	0	-	-	-	-	-	-	-
40	400	300	200	100	0	-	-	-	-	-	-
50	500	400	300	200	100	0	-	-	-	-	-
60	600	500	400	300	200	100	0	-	-	-	-
70	700	600	500	400	300	200	100	0	-	-	-
80	800	700	600	500	400	300	200	100	0	-	-
90	900	800	700	600	500	400	300	200	100	0	-
100	1000	900	800	700	600	500	400	300	200	100	0

$*VOC1 = (V_2-W)\ (Dm)\ 10 = A$

% Volatiles	% Water					
	0	20	40	60	80	100
			VOC 2 (g/liter)			
0	0	-	-	-	-	-
20	200	0	-	-	-	-
40	400	250	0	-	-	-
60	600	500	333	0	-	-
80	800	780	666	500	0	-
100	1000	1000	1000	1000	1000	0

$$**VOC2 = \frac{A(100)}{100 - Dm\ (W)\ /\ Dw}$$

Table 38. Volatile Organic Content (VOC) of a Solvent-Based Coating Containing Chlorinated (Exempt) Solvents

Determination of Volatile Organic Compound (VOC) Content of a Solvent-Based Coating Containing Chlorinated (Exempt) Solvents Using VOC1 and VOC2 (minus exempt solvent) Calculation.

% Volatile	% Exempt Solvent										
	0	10	20	30	40	50	60	70	80	90	100
	VOC1 (g/liter)*										
0	0	-	-	-	-	-	-	-	-	-	-
10	100	0	-	-	-	-	-	-	-	-	-
20	200	100	0	-	-	-	-	-	-	-	-
30	300	200	100	0	-	-	-	-	-	-	-
40	400	300	200	100	0	-	-	-	-	-	-
50	500	400	300	200	100	0	-	-	-	-	-
60	600	500	400	300	200	100	0	-	-	-	-
70	700	600	500	400	300	200	100	0	-	-	-
80	800	700	600	500	400	300	200	100	0	-	-
90	900	800	700	600	500	400	300	200	100	0	-
100	1000	900	800	700	600	500	400	300	200	100	0

*VOC1 = $(V_2 - W)$ (Dm) 10 = A

% Volatiles	% Exempt solvent					
	0	20	40	60	80	100
	VOC 2 (g/liter)					
0	0	-	-	-	-	-
20	200	0	-	-	-	-
40	400	250	0	-	-	-
60	600	500	333	0	-	-
80	800	780	666	500	0	-
100	1000	1000	1000	1000	1000	0

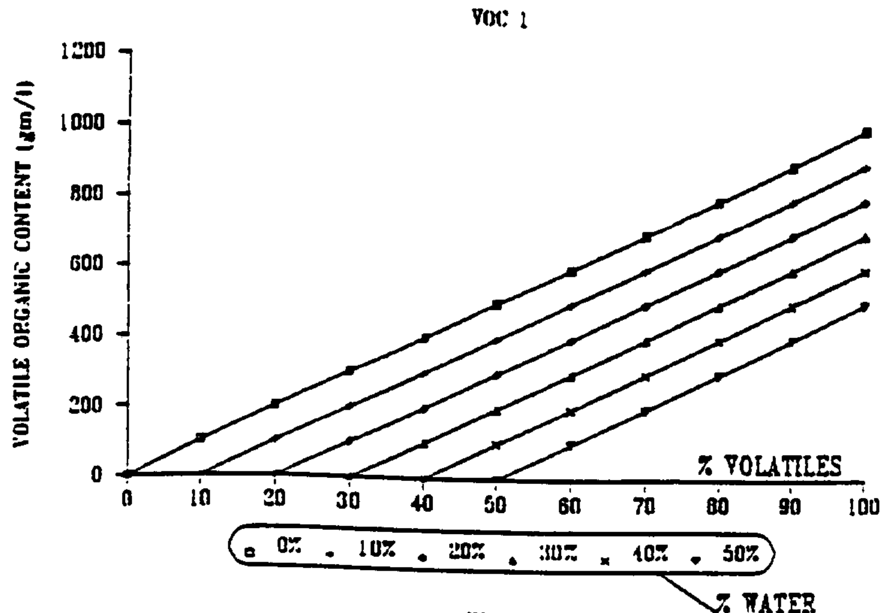
$$**VOC2 = \frac{A\ (100)}{100 - Dm\ (W)\ /\ Dw}$$

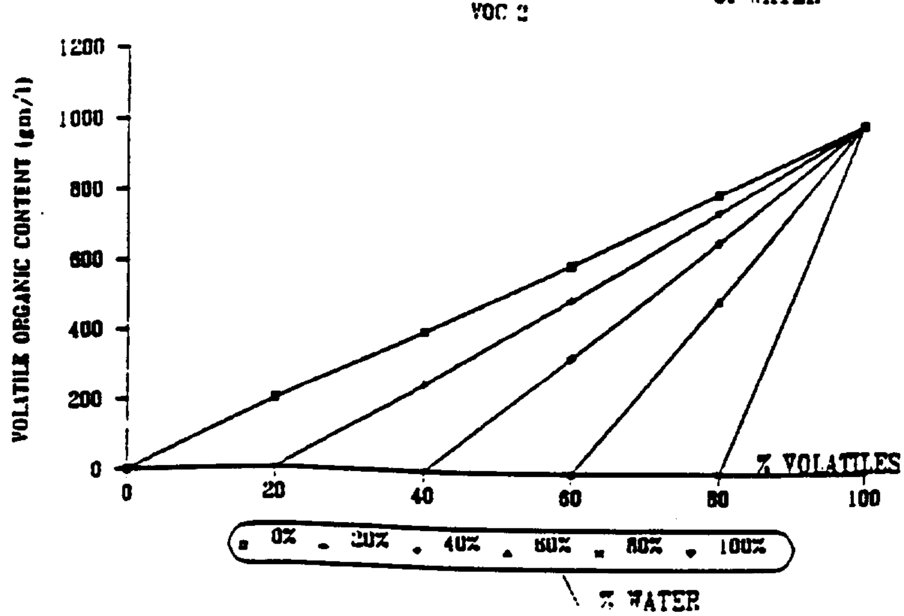
Figure 37. Volatile organic content comparison - VOC 1 versus VOC 2 (minus water)

FIGURE 37 Comparison of Volatile Organic Compound Content (VOC) determined using VOC1 and VOC2 (minus water calculations)

VOC1 = (volatile% - water%)(Dm)(10)

VOC2 = (VOC1 * 100) / (100-Dm*W/Dw)





G. Determination of Volatile Organic Compound (VOC) Content of a Water-based Coating using VOC1 and VOC2 (minus water)

The VOC Content of the original waterborne coating determined using ASTM D3960 was 176 g/liter. The manufacturer claimed to have diluted the coating with water only and the measured VOC increased to 265 g/liter. The original sample with a VOC of 176 g/liter was spiked at 17 and 28 percent water and the VOC content remeasured.

Discussion

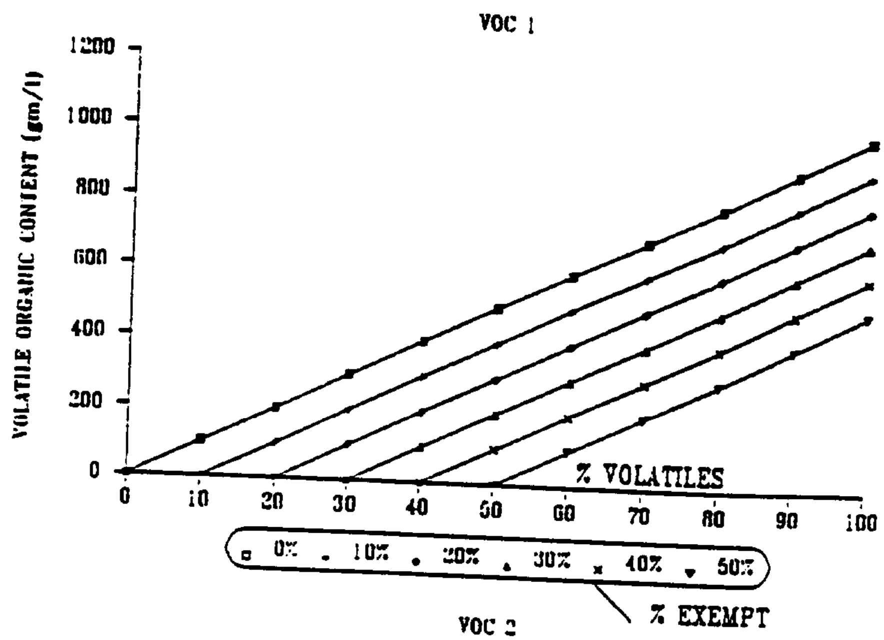
The VOC content of the original sample spiked with seventeen (17) percent water increased 13.7 percent to 204 g/liter. The VOC content of the original sample spiked with twenty-eight (28) percent water increased 25.4 percent to 236 g/liter. These VOC content numbers where determined using the conventional ASTM D3960 (minus water calculation). It appears that diluting with water does change (increase) the VOC content of a coating when using the ASTM D3960 (minus water) calculation. These numbers are given in **TABLE 39, The Effect of Increasing Water Content of a Waterborne Dip Tank Coating on the volatile Organic Compound (VOC) Content Using Conventional ASTM D3960** and displayed graphically in FIGURE 39.

Figure 38. Volatile organic content comparison - VOC 1 versus VOC 2 (minus exempt solvents)

FIGURE 38 Comparison of Volatile Organic Compound Content (VOC) Determined using VOC1 and VOC2 (minus exempt solvent calculations)

VOC1 = (volatile% - exempt%)(Dm)(10)

VOC2 = (VOC1 * 100) / (100-Dm*Ex/Dex)



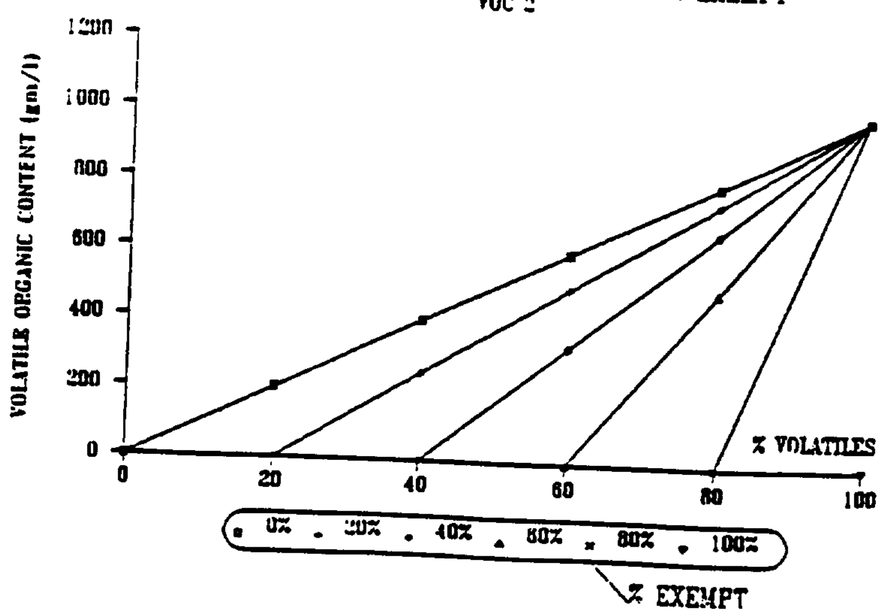


Table 39. The Effect of Increasing Water Content on the VOC of a Waterborne Dip Tank Coating

The Effect of Increasing Water Content of a Waterborne Dip Tank Coating on the Volatile Organic Compound (VOC) Content Using Conventional ASTM D3960.

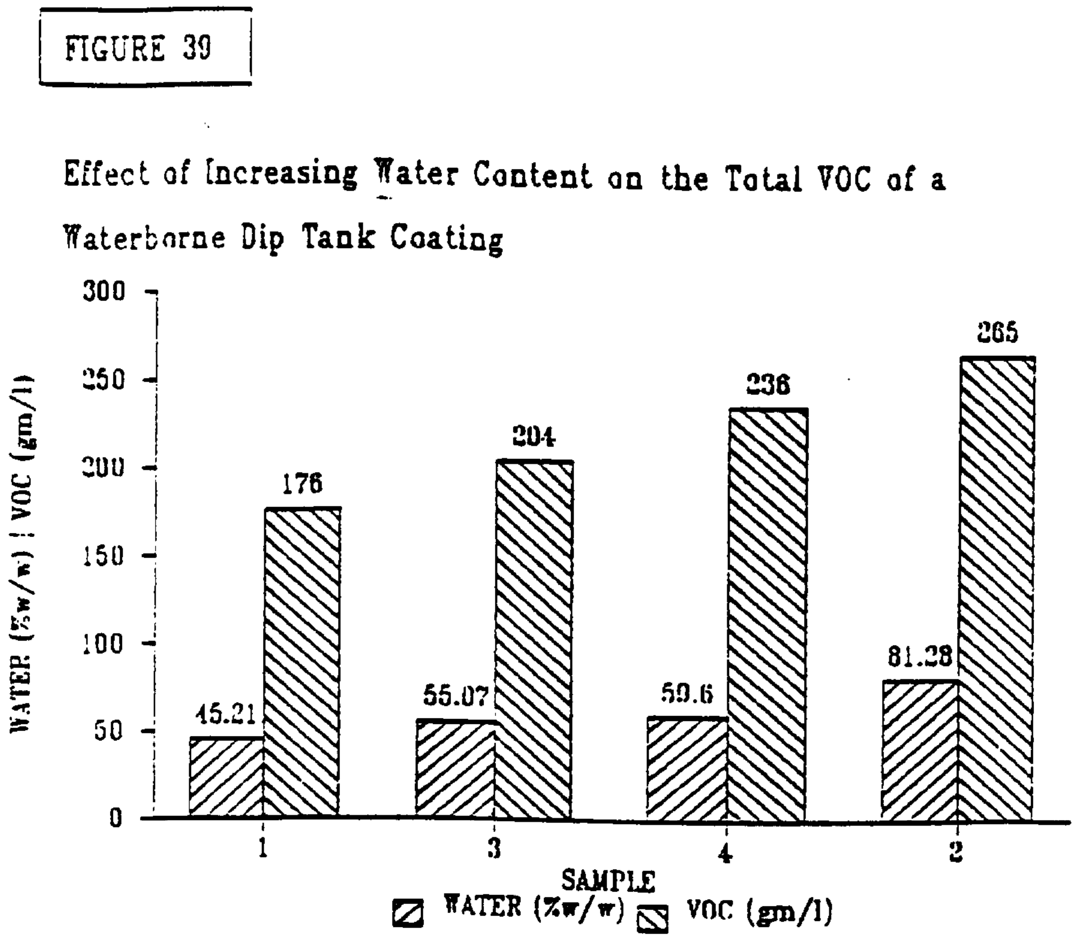
Sample	NV % (w/w)	Water % (w/w)	Density (g/ml)	VOC g/liter
1. Original coating	46.42	45.21	8.946	176
2. Diluted site coating	13.28	81.28	8.382	265
3. Original Coating spiked with 17% water	36.29	55.07	8.577	205
4. Original coating spike with 27% water	31.14	59.60	8.443	236

H. The effect of Water Entrapment in Non-Volatile (NV) Films on the Volatile Organic Compound (VOC) Content Measurement of Low VOC Waterborne Coatings

1. Summary of Test Method

The VOC content (g/liter) was measured for several low VOC waterborne ink samples. The water content of both the wet (liquid) samples and the non-volatile residues was measured using both Karl Fischer titration (ASTM D4017) and gas chromatography (modified D3792) techniques. The total non-volatile (NV) content of the wet waterborne coatings was measured using the standard ASTM D2369 testing protocol. The density of the wet samples was measured using ASTM D1475.

Figure 39. Volatile organic content as a function of increasing water content



2. Discussion

The VOC content (g/liter) of the low VOC waterborne ink samples measured using VOC1* of ASTM D3960 can result in a negative VOC value under some circumstances. Such instances can occur when the measured water content (either by KF titration or GC) is higher than the total volatile content measured using ASTM D2369. This "increased" water condition is due to water being trapped within the NV coating film, not allowing for a true volatile emission measurement. The negative VOC1 measurement occurs with coating samples in which the measured water content and total volatile content are extremely close. The NV coating film's ability to retain water may be a function of several variables. These include:

1) The affinity of the coating resin for very polar compounds (water).

2) An incorrect total dry film thickness (D.F.T.) of the coating in the aluminum pan (i.e. the coating was applied too thick)

   and

3) Improper coating substrata (i.e. different coatings diffuse into different substrata at different rates, hence leaving more or less water entrapped with the coating film depending on the particular substrata).

The ASTM D3960 calculation does not take into account these various discrepancies. In theory, a negative VOC1* and hence VOC2* is impossible and the VOC contents (g/liter) of the coating should be recorded as zero.

Example of the waterborne ink samples upon which the VOC1* measurement was negative are given in **TABLE 40 Volatile Organic Content (VOC) of Low VOC Waterborne Ink Samples.**

* VOC1 is defined in **TABLE 40.**

Figure 40. Accuracy estimates for VOC content

FIGURE 40

Accuracy Estimates for VOC Content of a Waterborne Photopolymer

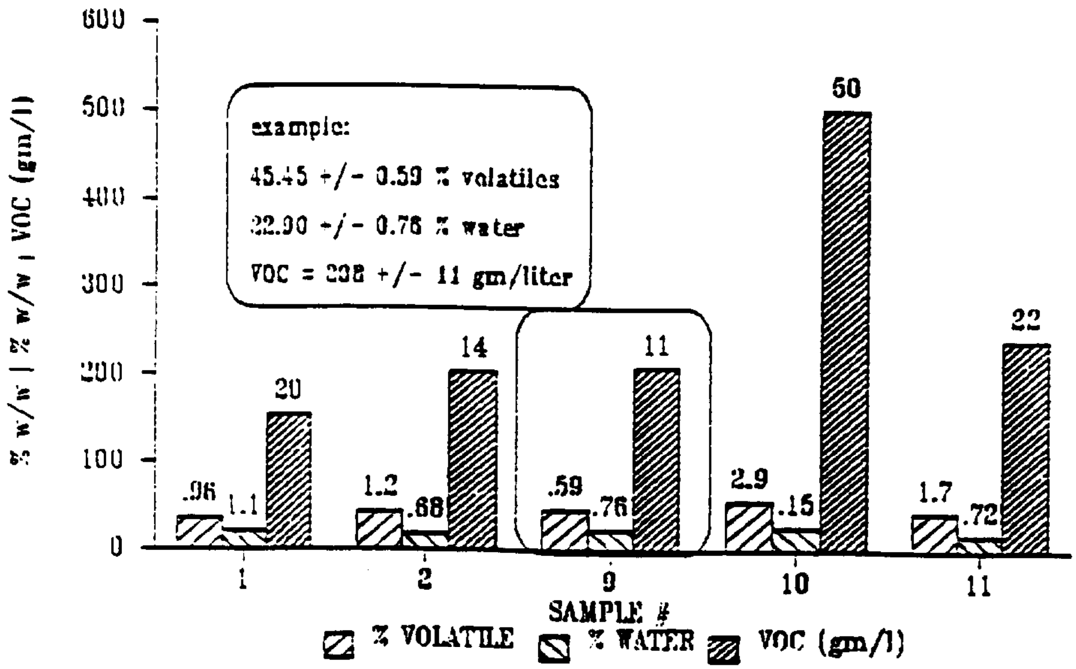


Table 40. Volatile Organic Content (VOC) of Low VOC Waterborne Ink Samples

Sample	Density (g/ml)	% water[1]	% volatile	VOC1[2] (g/liter)
1	1.136	65.77	65.51	-0.29
2	1.124	69.26	68.96	-0.34
3	1.031	61.41	60.72	-0.71
4	1.073	63.84	63.19	-0.70

1. % water reflects an average of KF and GC measurement

2. $VOC1 = (V_2 - W)\ (DM)\ 10.$
Where V_2= total volatile (%)
W= water content (%)
Dm= density of material (g/ml)

Figure 41. Water content by GC using proposed ASTM D3792

FIGURE 41 GC Water Content by using Proposed ASTM D3792

ARB Round Robin

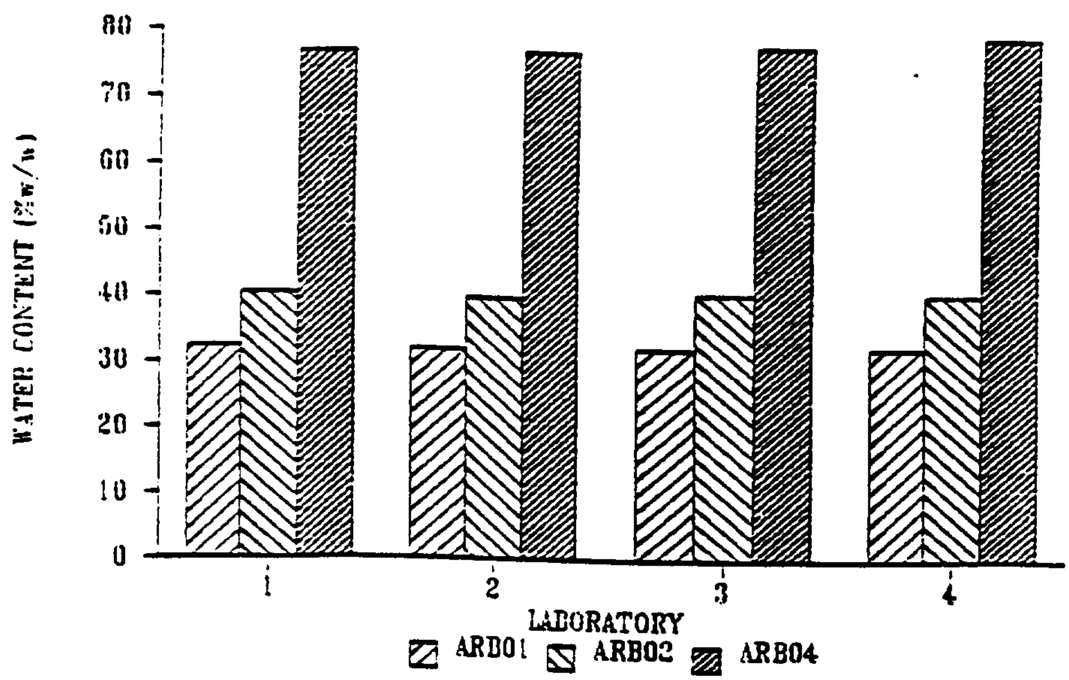
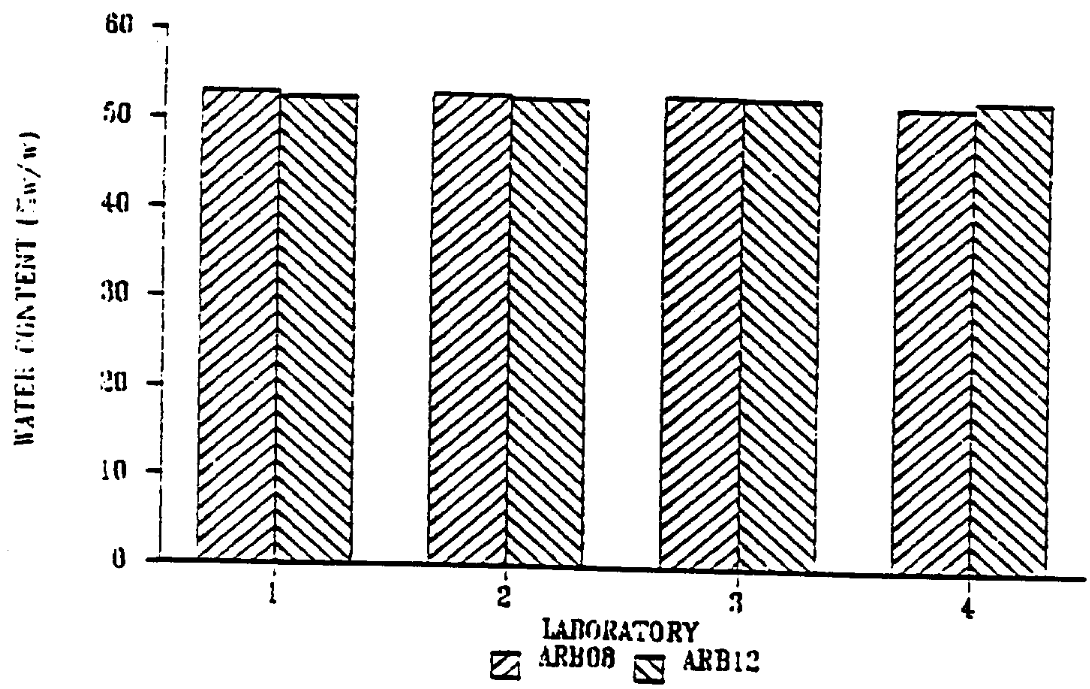


Figure 42. Water content by GC using proposed ASTM D3792

FIGURE 42 GC Water Content by using Proposed ASTM D3792

ARB Round Robin



11. ROUND ROBIN ON PROPOSED GC WATER -- Summary of Study on Determining Water Content of Water-reducible Paints by Direct Injection into a Gas Chromatograph (ASTM D3792)

The waterborne coating samples which were selected from the ARB/District compilation to execute the proposed modifications to ASTM D3792 included the following:

ARB Number	Description
01	High-Build water based terpolymer coating
02	Fire retardant roofing material (acrylic)
03	Water-based Wood Sealer
08	Test Sample Latex Paint #1
12	Test Sample Latex Paint #3

The various testing facilities which participated in the Round Robin study included the following:

A. Calcoast Analytical - ITL

B. Harlan and Associates

C. Bay Area Air Quality Management District (BAAQMD)

D. General Services Administration (GSA)

E. South Coast Air Quality Management District (SCAQMD)

Note: Although the same five (5) waterborne coating samples were also sent to the Air Industrial Hygiene Laboratory (AIHL) no data was received by the laboratory due to increased workload at AIHL.

11. ASTM D3792 - GC Water Continued

A. SUMMARY OF RESULTS -- ANALYSIS OF PRECISION USING ASTM E691

Proposed Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph - ASTM D3792

Summary of Precision

S_r (repeatability)	= 0.465	intra
r (2.8* Sr)	= 1.30	
S_R (reproducibility)	= 0.604	intra
R (2.8* S_R)	= 1.69	
Critical h (95%)	= 1.75	intra
Critical k (95%)	= 1.79	intra

12. ROUND ROBIN ON EXISTING KF WATER -- Summary of ASTM's Study on Determining Water in Automotive Finishes Using the Karl Fischer Method (ASTM D4017)

Four (4) automotive finishes were received by the laboratory for the analysis of water content using ASTM D4017 (KF). The samples received included:

Sample Number	Description
1	Water reducible topcoat
2	Water reducible topcoat
3	Water reducible topcoat
4	Water reducible electrocoat primer

The various testing facilities which participated in the Round Robin Study included the following:

A. Glidden

B. BASF _ SF

C. BASF - MD

D. SSECO

E. PPG

F. SCAQMD

G. Calcoast Analytical - ITL

H. BAAQMD

I. DuPont

J. D/L Labs

SUMMARY OF RESULTS -- ANALYSIS OF PRECISION USING ASTM E180-67*

Test Method for Water in Paints and Paint Materials by Karl Fischer Method - ASTM D4017

Summary of Precision

	Coef. of Var	DF	95% Range Factor	Sx Factor Relative Precision
A. Duplicate Runs				
Duplicate	5.11%	46	2.85	**14.55%**
B. Repeatability - Single Analyst				
Between Days within Laboratories	3.63%	23	2.93	**10.65%**
C. Reproducibility - Multi Laboratory				
Single Result Any Laboratory	18.36%	30	2.89	**54.35%**

13. ROUND ROBIN ON EXISTING VOC -- Summary of ASTM's Study on Determining Volatile Organic Compounds in Automotive Finishes Using the Existing Test Method (ASTM D2369)

Four (4) automotive finishes were received by the laboratory for the analysis of volatile content using ASTM D2369. The samples received included:

Sample Number	Description
1	Water Reducible topcoat
2	Water Reducible topcoat
3	Water Reducible topcoat
4	Water Reducible electrocoat primer

The various testing facilities which participated in the Round Robin Study included the following:

A. Glidden

B. BASF - SF

C. BASF - MD

D. SSECO

E. PPG

F. SCAQMD

G. Calcoast Analytical - ITL

H. BAAQMD

I. DuPont

J. D/L Labs.

13. ASTM D2369 - NV Content Continued

SUMMARY OF RESULTS -- ANALYSIS OF PRECISION USING ASTM E180-67*

Test Method for Volatile Content of Coatings - ASTM D2369

Summary of Precision

	Coef. of Var	DF	95% Range Factor	Sx Factor Relative Precision
A. Duplicate Runs				
Duplicate	0.21%	62	2.83	**0.60%**
B. Repeatability - Single Analyst				
Between Days within Laboratories	0.50%	31	2.89	**14.5%**
C. Reproducibility - Multi Laboratory				
Single Result Any Laboratory	1.18%	27	2.90	**3.43%**

* Actual data is included in Appendix E. Interlaboratory Round Robin Studies of Volatile Content of Coatings ASTM D2369.

DF: Degrees of freedom

Sx Factor: $\left[\frac{\Sigma DF * (\text{Coef of Var})^2}{\Sigma DF}\right]^{1/2}$

14. ROUND ROBIN ON PROPOSED GC -- Summary of Study on the Proposed Method for Determination of Dichloromethane and 1, 1, 1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Ghromatograph (ASTM D4457)

The solvent-based coating samples which were selected from the ARB/District complication to execute the proposed modifications to ASTM D4457 included the following:

ARB Number	Description
10	Traffic marking paint
22	Flat black lacquer
24	Unsaturated polyester resin
72	Ripley resin/ electrical insulating resin
80	No VOC stain

The various testing facilities which participated in the Round Robin study included the following:

A. Calcoast Analytical - ITL

B. Harlan and Associates

C. Bay Area Air Quality Management District (BAAQMD)

D. General Service Administration (GSA)

E. South Coast Air Quality Management District (SCAQMD)

Note: although the same five (5) solvent-based coating samples were also sent to the Air Industrial Hygiene Laboratory (AIHL) no data was received by the laboratory due to an increased work load at AIHL.

14. ASTM D4457 - Exempt Solvents by GC Continued

SUMMARY OF RESULTS -- ANALYSIS OF PRECISION USING ASTM E691

Proposed Test Method for the Determination of Dichloromethane and 1, 1, 1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph - ASTM D4457

Summary of Precision

	DCM	TCA
S_r (repeatability)	= 0.363	0.409
r (2.8* Sr)	= 1.017	1.144
S_R (reproducibility)	= 2.465	3.022
R (2.8* S_R)	= 6.901	8.491
Critical h (95%)	= 1.49	1.49
Critical k (95%)	= 1.73	1.73

* Actual data together with chromatograms are included in Appendix E. Interlaboratory Volatile Organic Content (VOC) Round Robin Study Determination of Dichloromethane and 1, 1, 1 Trichloroethane in Paints and coatings by Direct Injection into a Gas Chromatograph - ASTM D4457

15. ROUND ROBIN ON EXISTING DENSITY -- Summary of ASTM's Study Using the Existing Method to Determine the Density of Automotive Finishes (ASTM D1475)

Four (4) automotive finishes were received by the laboratory for the analysis of density using ASTM D1475 the samples included:

Sample Numbers	Descriptions
1	Water Reducible topcoat
2	Water Reducible topcoat
3	Water Reducible topcoat
4	Water Reducible electrocoat primer

The various testing facilities which participated in the Round Robin Study included the following:

A. Glidden

B. BASF - SF

C. BASF - MD

D. SSECO

E. PPG

F. SCAQMD

G. Calcoast Analytical - ITL

H. BAAQMD

I. Dupont

J. D/L Labs.

15. ASTM D1475 - Density Continued

SUMMARY OF RESULTS -- ANALYSIS OF PRECISION USING ASTM E180-67*

Test Method for Density of Paint, Varnish, and Related Products - ASTM D1475

Summary of Precision

	Coef. of Var	DF	95% Range Factor	Sx Factor Relative Precision
A. Duplicate Runs				
Duplicate	0.07%	68	2.82	**0.19%**
B. Repeatability - Single Analyst				
Between Days within Laboratories	0.14%	34	2.88	**0.40%**
C. Reproducibility - Multi Laboratory				
Single Result Analytical Laboratory	1.08%	30	2.89	**3.12%**

* **Actual data is included in Appendix E. Interlaboratory Round Robin Studies of Density of Paint, Varnish, and Related Products.**

16. CRITIQUE OF EXISTING VOC -- Experimental and Theoretical Flaws in the Existing Method to Determine the Volatile Organic Compound Content of Paints and Related Coatings (ASTM D3960)

Experimental as well as theoretical evaluation of the application of D3960 reveals that the term "exempt" solvent inaccurately portrays the role of water or chlorinated solvents. Coatings having identical volatile organic content with differing solids levels result in widely varying final VOC results. The use of high-solids coatings is advantageous while the use of low solids dispersion coatings is penalized although the solvents used in the low solids material may be entirely "exempt".

See Figures 36, 37, and 38.

Additionally, the end user of a compliant coating may add exempt solvents prior to application to give a non-compliant coating.

17. ASTM COMMITTEE D-1 MEETING in Fort Lauderdale, Florida, January 1991

On January 21 and 22, 1991 two (2) representatives from Calcoast Analytical - ITL Labs attended the ASTM Committee D-1 meeting in Ft. Lauderdale, Florida. The following are comments from that meeting.

A. Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph - ASTM D3792.

Calcoast Analytical - ITL Labs placed a negative vote on ASTM'S D0103 (90-3) letter ballot for Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph - ASTM D3792.

On October 22, 1991, Calcoast Labs received a letter from S. Orthey ASTM Staff Manager to Hiroshi Fujimoto ASTM D01.21 Subcommittee Chairman concerning the negative vote. Mr. Fujimoto contacted Calcoast Labs in January 1991 by telephone and said that negative vote was well received and that existing ASTM D3792 specification would be revised. The negative vote by Calcoast Labs was primarily based on some of the terminology in the existing ASTM specification. In particular, in Section 5. Apparatus, paragraph 5.1 Gas Chromatograph reads as follows "Any gas -liquid chromatographic instrument having a detector may be used." A copy of Calcoast Analytical - ITL letter which was sent to ASTM Subcommittee D0121 Chairman H. Fujimoto and ASTM'S response is included at the end of this section. While ASTM did agree to revise the section describing the detector used for analysis, they gave no indication as to the adoption of Calcoast Labs other proposed modifications. Mr. Fujimoto asked that proposed modifications along with Calcoast Labs accumulated Round Robin data using those modification be sent to ASTM Subcommittee D01.21 for review. These Round Robin results compiled for CARB are included with this report.

B. ASTM'S Round Robin #2 on Determining VOC of Multi-component Paints & Coating - ASTM D01.21.27

The purpose of the Round Robin was to describe a standard procedure for preparing samples of multi-component paints for solids, weight per gallon and water determination, in order to calculate VOC. A copy of the ASTM Practice Draft is enclosed at end of this section in this report. Calcoast Labs has not yet had a chance to use and evaluate the ASTM procedure since it was submitted to Calcoast Labs in January 1991 at the ASTM meeting.

C. New Approaches in VOC Measurement - D01.21.24

Dr. R. Jayanty of Research Triangle Institute (RTI) submitted his test method for measuring the Volatile Organic Content (VOC) of coatings using charcoal tube entrapment. Dr. R Jayanty pointed out that the RTI proposed method would not work for systems containing methanol due to the low affinity of methanol for activated charcoal. Mr. Fujimoto expressed his concern that the method would be an invalid way of measuring the VOC of automotive finishes since many contain methanol. ASTM D01.21.24 did not approve the RTI proposed test method.

D. Test Method for Water in Paints and Paint Materials by Karl Fischer Method - ASTM D4017 D01.21.54 by the ASTM Subcommittee

Currently, the only revision proposed of ASTM D4017 is the addition of the 1-ethylpiperidine catalyst. The use of this catalyst was approved by D01.21.54 and is now in print. Mr. Fujimoto invited Calcoast Labs to submit their data involving less toxic, alternative solvents for water content by Karl Fischer. The KF results compiled for CARB are included with this report.

E. Revision of Test Method For Determination of Dichloromethane and 1, 1, 1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph - ASTM D4457 - D01.21.54.

The revision of exempt solvent content by GC (ASTM D4457) was cancelled by Mr. H. Fujimoto due to absence of the chairman. Mr. Fujimoto did invite Calcoast Labs to submit their proposed method and Round Robin results obtained. These Round Robin results complied for CARB are included with this report and can be released to ASTM D01.21.54 for review pending CARB's approval.

F. VOC Content of Aerosols - D01.27.27A.

A Round Robin study was conducted by ASTM for VOC content of water and solvent-based aerosols using BAAQMD Method 36. D01.27.27A approved the BAAQMD Method 36 for VOC of solvent-based aerosols. However, the ASTM subcommittee felt additional work need to be done on water-based systems due problems releasing propellant and residual propellant's (dimethyl ether) solubility in water (less than six (6) percent). Calcoast Labs agreed to participate in an additional study of the above problems and a second Round Robin Study.

18. SUMMARY AND CONCLUSIONS

A. Summary of Reproducibility (Relative %) using the Existing ASTM Test Methods Versus Calcoast Labs Proposed Methods for the Determination of Volatile Organic Content (VOC) of Paints and Related Coatings (ASTM D3960) Evaluated Through the Interlaboratory Round Robin Studies

ASTM Method Number	Method	Version of Test Method	Relative Reproducibility
1. D3792-86	Water	1. Currently Published by ASTM	7.5%
		2. ASTM'S Automotive Finishes Interlaboratory Round Robin Study using Existing Test Method	7.8%
		3. Calcoast Labs Interlaboratory Round Robin Study using Proposed Method	1.8%
2. D4017	Water (KF)	1. Currently Published by ASTM	15.0%
		2. ASTM'S Automotive Finishes Interlaboratory Round Robin Study using Existing Test Method	5.0%
		3. Use of Existing Test Method is Recommended by Calcoast Labs. *	-
3. D2369-81	Non-Volatile (NV) Content	1. Currently Published by ASTM	4.7%**
		2. ASTM'S Automotive Finishes Interlaboratory Round Robin Study using Existing Test Method	3.4%
		3. Use of Existing Test Method is Recommended by Calcoast Labs.	-

ASTM Method Number	Method	Version of Test Method	Relative Reproducibility
4. D4457-85	Exempt Solvent (GC)	1. Currently Published by ASTM	
		a. DCM[1]	17.9%
		b. TCA[2]	8.1%
		2. Calcoast Labs Interlaboratory Round Robin Study using Proposed Method	
		a. DCM	1.7%
		b. TCA	1.7%
		3. ASTM'S Automotive Finishes Interlaboratory Round Robin Study using Existing Test Method	Not Applicable All Coatings Tested were Water-Based
5. D1475-60	Density	1. Currently Published by ASTM	1.5%
		2. ASTM'S Automotive Finishes Interlaboratory Round Robin Study using Existing Test Method	3.1%
		3. Use of Existing Test Method is Recommended by Calcoast Labs	-

* Calcoast Labs recommends the use of an automated (microprocessor) controlled Karl Fischer Titration for greater precision, accuracy and reproducibility. Less toxic solvents such as methanol can be used with most waterborne systems with the same precision accuracy, and reproducibility as that when using the specified pyridine solvent.

**Test method used including using a temperature of 110°C for sixty (60) minutes.

[1]DCM - Dichloromethane
[2]TCA - 1, 1, 1 Trichloroethane

B. Conclusions

1. Water Content Using Gas Chromatography - ASTM D3792

a. Modifications Proposed

Calcoast Analytical Labs proposes the modifications shown in Appendix B. When they were used in the Interlaboratory Round Robin Study the relative reproducibility was 1.8%, compared to the existing method's 7.8% (and 7.5% as published by the ASTM). The figures are shown in Figure 43.

b. Remarks

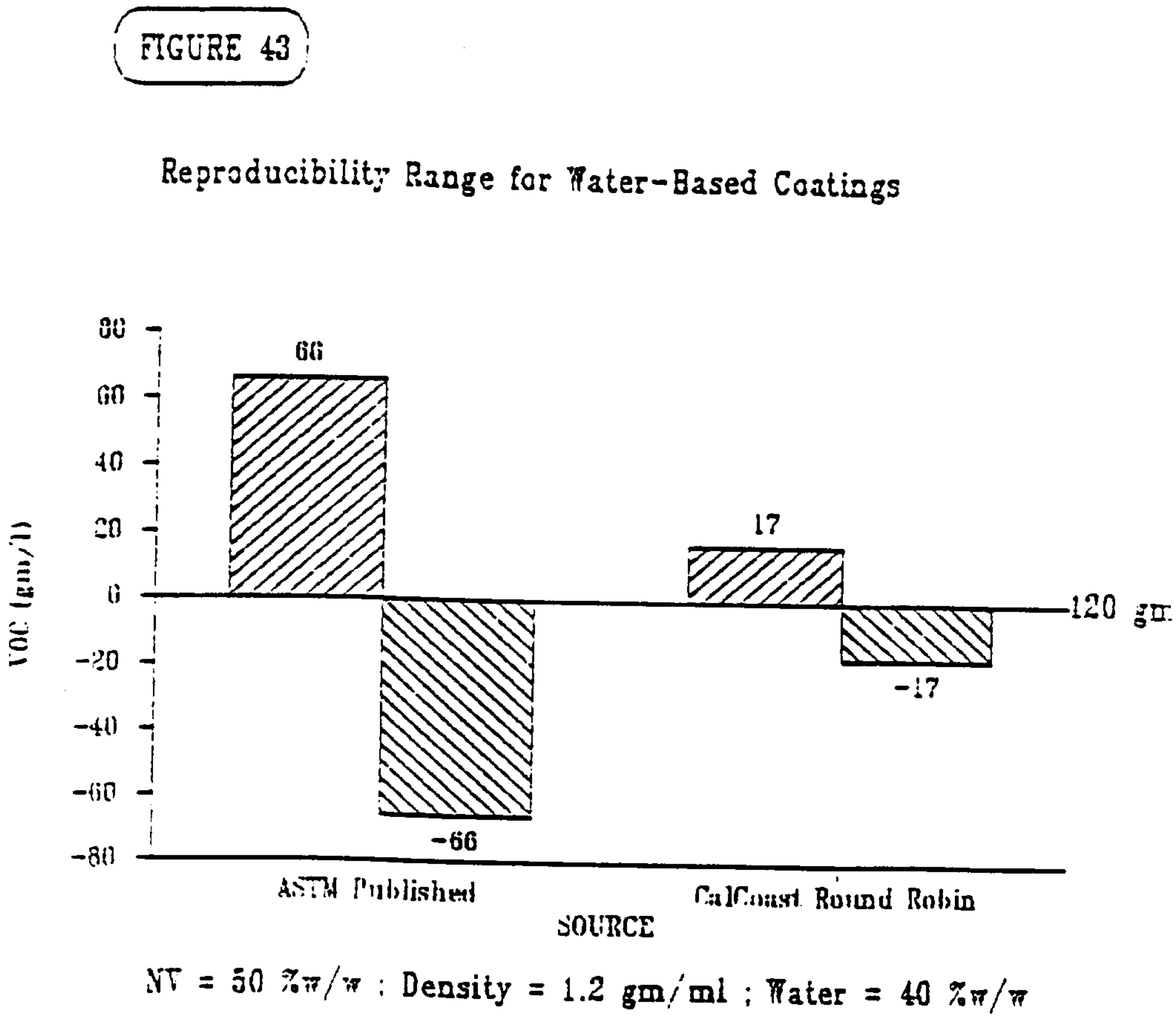
Calcoast Analytical Labs feels that there are two primary reasons for the improved reproducibility using the modifications; firstly, the modifications themselves, and secondly, factors such as the condition of the equipment, the expertise of the operator, and the familiarity of analyzing water content with a gas chromatograph.

c. Cross-references

For further information, see:

Section 3:	Proposed GC Water
Section 4:	Proposed vs. Existing GC Water
Section 11:	Round Robin on Proposed GC Water

Figure 43. Reproducibility Range for Water-Based Coatings



B. Conclusions: Continued

2. Water Content using Karl Fischer Titration - ASTM D4017

a. Modifications Proposed

Calcoast Labs strongly recommends that water content be determined using either a microprocessor controlled KF titrator or a manual titrator with an experienced operator. Under those conditions, it is easy to attain relative reproducibility (percent) of 5.0% and lower.

b. Remarks

In the opinion of Calcoast Labs, the published relative reproducibility (15%) is much too high, and values of 5% or lower can be obtained relatively easily. ASTM's automotive finishes Round Robin produced a value of 5.0%.

The primary factors in obtaining lower numbers appear to be the type of Karl Fischer titrator used, and the level of operator skill. In interlabortory testing, the numbers approached 15.0% when an unskilled operator was using a manual KF titrator. An experienced operator analyzing the same coating samples obtained 5% reproducibility. A microprocessor controlled KF titrator used on the same samples obtained reproducibility of 1.5% whether or not the operator was experienced with the instrument. The microprocessor controlled titrator requires a much lower level of operator experience and therefore is much less operator dependent.

c. References

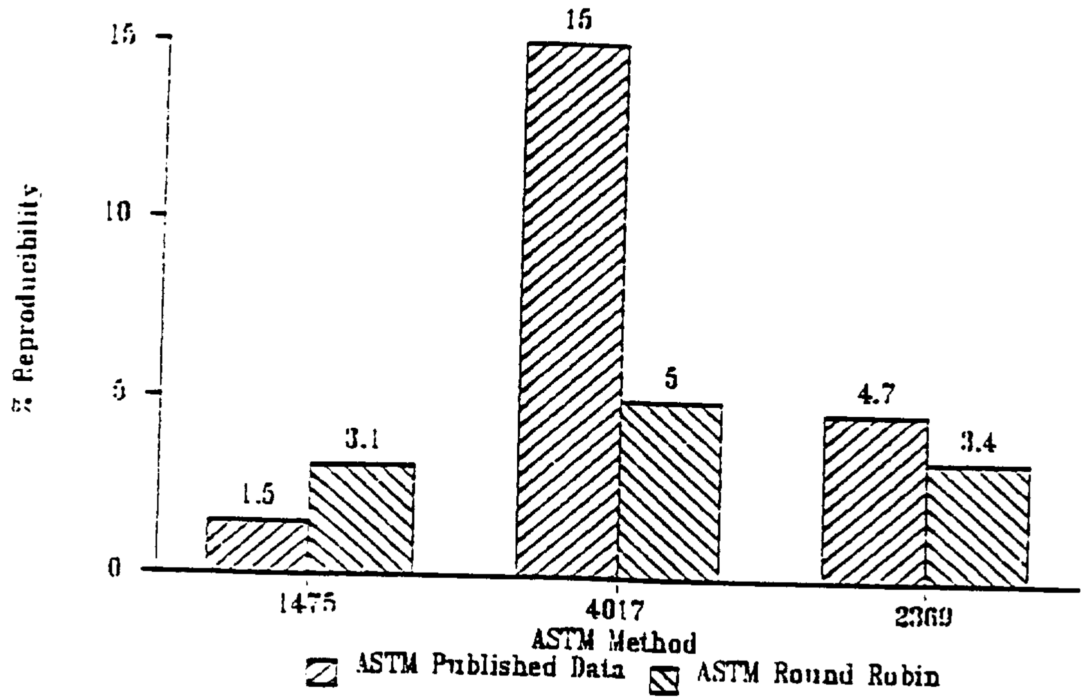
For further information, see:

Section 5: Experimental KF Water
Section 12: Round Robin on Existing KF Water

Figure 44. Comparison of Reproducibility Range of ASTM Published Data versus ASTM Round Robin for Density, KF Water, and Non-Volatile Content

FIGURE 44

Comparison of Reproducibility Range of ASTM Published Data versus ASTM Round Robin for Density, KF Water, and Non-Volatile Content



ASTM D1475 - Density of Coatings

ASTM D4017 - Water Content by Karl Fischer Titration

ASTM D2369 - Total Volatile Content

B. Conclusions: Continued

3. Non-volatile (NV) Content - ASTM D2369

a. Modifications Proposed

In the opininon of Calcoast Labs, the relative reproducibility (percent) of the existing test specification is within the expected error range for measuring the non-volatile (NV) content of most coating samples.

The published relative reproducibility of the existing test specification is 4.7%. ASTM's automotive finishes Round Robin produced a relative reproducibility of 3.4% using the existing test method. These numbers are given in Figure 44.

b. Remarks

During intralaboratory testing it was determined that by using a microwave oven, the NV relative reproducibility numbers of 4.7% and lower can be obtained in 30 minutes, versus 60 minutes using a convection oven. The microwave oven works well for most systems, but some present problems, such as those containing aluminum pigmentation.

c. References

For further information, see:

Section 6: Experimental VOC
Section 13: Round Robin on Existing VOC

B. Conclusions: Continued

4. Exempt Solvent Content using Gas Chromatography - ASTM D4457

a. Modifications Proposed

Calcoast Labs strongly recommends that the proposed test method modifications given in Section 7 of this report should be adopted, in order to obtain a substantial reduction from the published relative reproducibility (percent) numbers.

The published relative reproducibility of the existing test specification is **17.9%** for dichloromethane and **8.1%** for 1, 1, 1 trichloroethane.

The relative reproducibility numbers obtained using Calcoast Analytical Labs proposed modifications evaluated through the interlaboratory Round Robin study were **1.7%** for both dichloromethane and 1, 1, 1-trichloroethane. These numbers are given in **FIGURE 46**.

Calcoast Labs feels that the large decrease in relative reproducibility (percent) for both dichloromethane and 1, 1, 1 trichloroethane using the proposed method is due to instrumental and procedural changes as well as operator expertise.

b. Remarks

c. References

For further information, see:

Section 7: DCM and TCA by Proposed GC
Section 8: Proposed vs. Existing GC
Section 14: Round Robin on Proposed GC

B. Conclusions: Continued

5. Density - ASTM D1475-60

a. Modifications Proposed

In the opinion of Calcoast Analytical Labs, the existing ASTM D1475 testing specification need not be modified, since it is within the expected relative percent reproducibility error range for measuring the density of most coatings. These numbers are given in **FIGURE 44**.

b. Remarks

The level of operator expertise required for the existing ASTM D1475 is relatively low. The cost of the equipment needed is also relatively low. At present, no cheaper, easier methods are available which are sufficient for measuring the density of most coatings.

The relative reproducibility of the existing test specification is 1.5%. There are test methods, such as a gas pycnometer, which may yield a lower relative percent reproducibility.

Measuring the density of certain types of coatings, such as gels and powder coatings, does present some problems. The observed density depends greatly on whether it is measured loose or packed.

c. Cross-references

For further information, see:

Section 9: Density by Existing Method
Section 15: Round Robin on Existing Density Method

B. **Conclusions:** Continued

6. **Volatile Organic Content (VOC) - ASTM D3960**

a. Volatile Organic Content (VOC) Reproducibility Range for Solvent-Based Coatings containing No Exempt Solvents

The relative reproducibility VOC range for a solvent-based coating containing no exempt solvents with a non-volatile (NV) content of 50.00% (w/w), a density of 1.2 gm/ml, and a VOC of 600 g/l is 600±39 g/l using the ASTM published reproducibility numbers. The same coating as evaluated through an ASTM Round Robin Interlaboratory Study was 600±46 g/l. These numbers are displayed graphically in Figure 45. Note: with this coating VOC 1 = VOC 2.

b. Volatile Organic (VOC) Reproducibility Range for Solvent-Based coatings Containing Exempt Solvents using ASTM D4457 (Exempt solvent Content by GC)

The VOC relative reproducibility range for a solvent-based coating containing both dichloromethane and 1, 1, 1 Trichloroethane at 20.00% w/w levels, a non-volatile content of 50.00% w/w, and a density of 1.2 g/ml for VOC1 was 120±91 g/l and 231±209 g/l for VOC2.

The VOC relative reproducibility range for the same proposed test method was 120±22 g/l for VOC1 and 231±42 g/l for VOC2. These numbers are displayed graphically in Figure 46.

c. Volatile Organic (VOC) Reproducibility Range for Water-based Coating using ASTM D3972 (Water Content by GC)

The VOC relative reproducibility range for a water-based coating having a water content of 40.00% w/w, and density of 1.2 g/ml using the published ASTM data was 120±66 g/l for VOC1 and 231±126 g/l for VOC2.

The VOC relative reproducibility range for the same coating using Calcoast Labs proposed test method was 120±17 g/l for VOC1 and 231±33 g/l for VOC2. These numbers are displayed graphically in Figure 47.

d. Cross-references

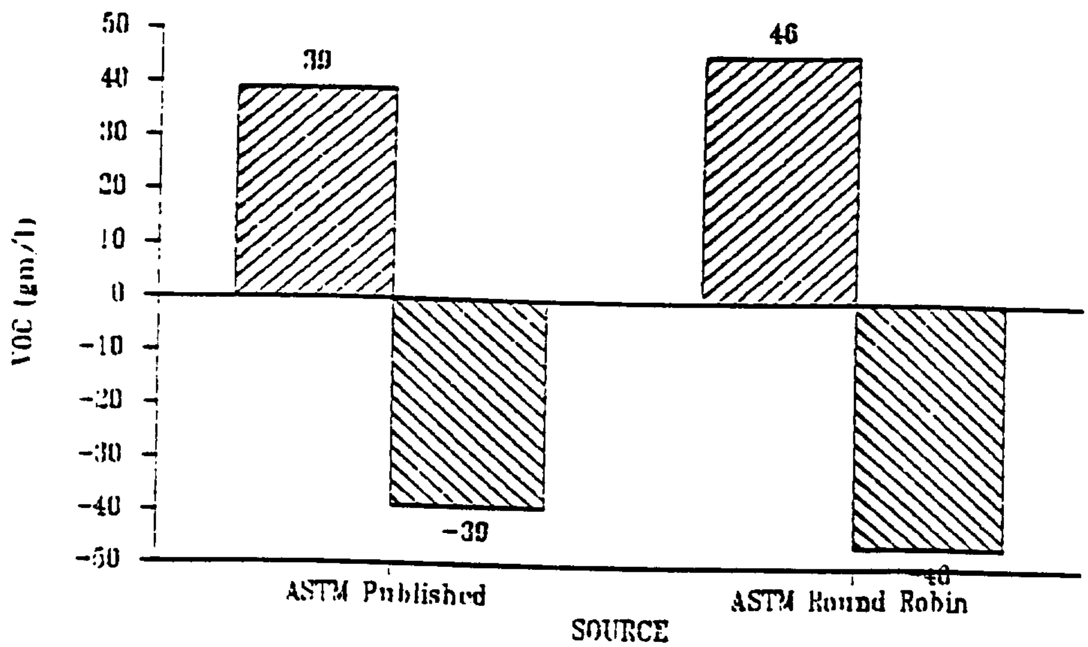
For further information, see:

Section 10: Experimental VOC
Section 16: Critique of Existing VOC

Figure 45. Volatile Organic Content (VOC) Reproducibility Range for Solvent-Based Coatings with no exempt Solvents

FIGURE 45

Volatile Organic Content (VOC) Reproducibility Range for Solvent-Based Coatings with No Exempt Solvents

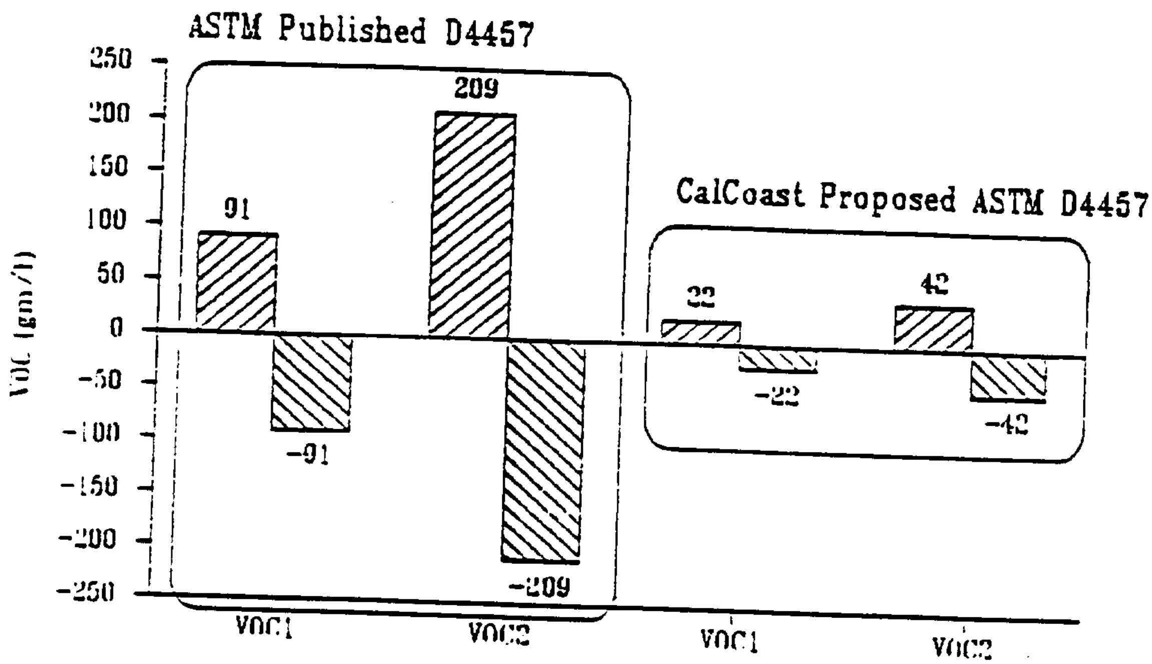


Coating Parameters: NV = 50 %w/w ; Density = 1.2 gm/ml ; VOC = 600 gm/l

Figure 46. Volatile Organic Content (VOC) Reproducibility Range for Solvent-Based Coatings with Exempt Solvents

FIGURE 46

Volatile Organic Content (VOC) Reproducibility Range for Solvent-Based Coatings with Exempt Solvents

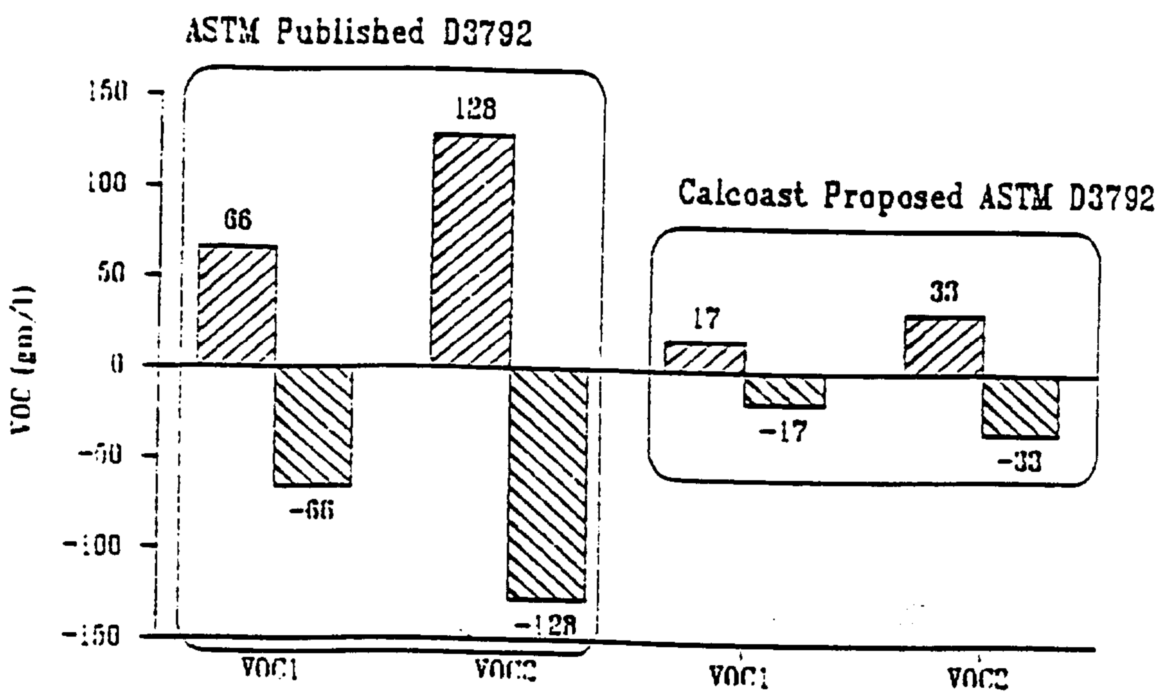


Coating Parameters: NV = 50 %w/w ; Density = 1.2 gm/ml ; DCM = 20 %w/w ; TCA = 20 %w/w ; VOC1 = 120 gm/l ; VOC2 = 231 gm/l

Figure 47. Volatile Organic Content (VOC) Reproducibility Range for Water-Based Coatings

FIGURE 47

Volatile Organic Content(VOC) Reproducibility Range for Water-Based Coatings



Coating Parameters: NV = 50 %w/w ; Density = 1.2 gm/ml ;
Water Content = 40 %w/w ; VOC1 = 120 gm/l ; VOC2 = 231 gm/l

19. RECOMMENDATIONS:

Calcoast Labs has proposed revisions to ASTM test methods D3792 (GC water) and D4457 (exempt solvents by GC) incorporated in ASTM D3960 Determination of Volatile Organic Compound (VOC) Content of Paints and Related Coatings. Through Interlaboratory Round Robin Studies using the proposed test methods, Calcoast Labs has reduced the relative reproducibility of the water content by GC from 7.5 to 1.8%. Using the proposed test method for exempt solvents, the relative reproducibility has been reduced from 17.9% for dichloromethane and 8.1% for 1, 1, 1 trichloroethane to 1.7% for each.

The above relative reproducibility numbers using the test methods proposed by Calcoast Labs allows the California Air Resources Board and the various air quality management districts to enforce a limit of less than fifteen (15) percent on the reproducibility of VOC content of waterborne coatings and less than eighteen (18) percent for solvent-based coatings containing exempt solvents. Note: these numbers are calculated using the published maximum relative reproducibility errors using the existing ASTM D2369 (NV) and ASTM D1475 (density) test methods and the final VOC (g/l) value is presented as VOC2 (minus water or exempt solvents).

The existing ASTM test methods allow a relative VOC (g/l) relative reproducibility of 55% for water-based coatings and 90% for solvent-based coatings containing exempt solvents using the VOC2 (minus water and exempt solvent calculation).

While the test methods proposed by Calcoast Labs offer a considerable reduction in maximum deviation in the VOC content determination of coatings, much work still needs to be done. Areas which need further exploration and attention include:

A. Non-volatile (NV) Content of waterborne aerosols

B. Accurate method for measuring water content of aerosols

C. Volatile Organic Compound (VOC) speciation by Mass Spectroscopy.

D. Further Round Robin Studies using ASTM D2369 (NV), ASTM D3792 (GC water), ASTM D4017 (KF water), ASTM D1475 (density), and ASTM D4457 (exempt solvents by GC) to evaluate the existing relative reproducibility numbers published in those test methods.

19. **RECOMMENDATIONS:** Continued

It is the opinion of Calcoast Labs that while some of the ASTM test methods incorporated into the ASTM D3960 (VOC) calculation contain instrumental and procedural flaws, errors introduced by equipment and personnel must also be prevented.

Laboratories not equipped either with the proper instrumentation or experienced personnel for testing the VOC of coatings should not be included in the interlaboratory Round Robin or VOC testing of coatings in general without some type of certification.

The National Voluntary Laboratory Accreditation program (NVLAP) offered by the National Institute of standards and technology provides a reasonable system for quality assurance. Laboratory credibility is monitored through participation in the Collaborative Testing Service (CTS) which includes all of the ASTM procedures applicable to paint testing. Calcoast Labs is one of only four laboratories currently accridited by NIST in the United States, however many laboratories participate in the CTS program.

A certification agency for evaluating the laboratory proficiency in VOC content testing should be put in effect to screen out laboratories which are testing coatings incorrectly.

Pat Fairley, Lab Director

20. APPENDICES

A. Definitions

1. **ASTM D1475**

   Density - weight per unit volume. Reported as grams/milliliter or pounds/gallon.

2. **ASTM D2369**

   Volatile Content - Portion of coating removed by exposure to heating at 110°C for 60 minutes. Reported as weight %.

   Non-Volatile Content - Portion of coating remaining after exposure to heating at 110°C for 60 minutes.

3. **ASTM D3792**

   Response Factor - Sensitivity of detector response to water compared to isopropanol

   Diluent - Carrier solvent used to help disperse coating (DMF)

4. **ASTM D3960**

   Volatile Organic Compound Content (VOC) - Material besides exempt solvents (water, chlorinated solvents) released during coating cure.

   VOC 1 = (total volatiles (%)-exempt solvents (%)) *D*10

   VOC 2 = (100 * VOC 1) / (100 - D_c E/D_E); final

   VOC including "minus exempts" calculation. D_c = Density of coating (gm/ml); D_E = Density of exempt solvent (gm/ml); E = % exempt solvent

5. ASTM D4017

Solvent - solvent system in which the titration is performed. (methanol, dimethylformamide, formamide, pyridine)

6. ASTM D4457

PGME - Propylene glycol methyl ether; an alternative diluent chosen due to is effective solubility of a broad spectrum of coating resins

THF - Tetrahydrofuran; an alternative internal standard chosen due to good FID response, absence in coating samples, and good retention time.

20 B. Proposed Modification to ASTM D3792 - Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph

Parameter	ASTM D3792	Modification
a. Detector Temperature	240°C	240°C
b. Injection Temperature	200°C	240°C
c. Carrier Gas flow rate mls/min	50	36 helium recommended
d. Column		
1. Type	PORAPAC Q	PORAPAC Q
2. Length	4 ft	8 ft
3. Mesh	60/80	80/100
e. Column temperature °C		
1. Initial	80	75
2. Final	170	210 12 min. hold
3. Program Rate	30C/min	12C/min.
f. Liquid charging Device	10 or 25 ul syringe	5 ul
g. Sample Preparation		
1. Size	0.6g	1.2g
2. Internal Standard	0.2g	0.5g
3. Diluent (DMF) amount	2 mls	6 mls

20 C. Proposed Modifications to ASTM D4457 - Determination of Dichloromethane and 1, 1, 1 Trichloroethane in Paints and Coatings by Direct Injection Into a Gas Chromatograph

Parameter	ASTM D4457	Proposed Modification
a. Detector		
1. Type	Thermal Conductivity or Flame Ionization Detector (FID)	FID required
2. Temperature	250°c	240°C
b. Injector Temperature		
c. Carrier Gas Flow Rate mls/min.	30	30
d. Column		
1. Type	Porous Polymer	10% sp-2100
2. Length	4' x 1/8"	20' x 1/8"
3. Mesh	80/100	80/100
e. Column Temperature °C		
1. Initial	100	55 (3 min.)
2. Final	230 (8 min.)	185 (15 min.)
3. Program Rate	8 °c/min	6 °C/min
f. Sample Preparation		
1. Size	5.0g	1.2g
2. Internal Standard	1-propanol (2g)	THF (0.5g)
3. Diluent	DMF (16g)	PGME (5g)

20. D. Coating Samples Collected by the California Air Resources Board

ARB/DISTRICT/CALCOAST SAMPLE COMPILATION

SC = SOUTH COAST AQMD
MTS = SAN DIEGO COUNTY APCD (MONITORING AND TECHNICAL SERVICES)

ARB NUMBER	DISTRICT NUMBER	SAMPLE DESCRIPTION
ARB-01	N/A	HIGH-BUILD WATERPROOF TERPOLMER COATING
ARB-02	N/A	FIRE RETARDANT WATERPROOF ROOFING MATERIAL (ACRYLIC)
ARB-03	N/A	CLEAR ASPHALT SEALER
ARB-04	N/A	WATER-BASED WOOD SEALER
ARB-05	N/A	MASONRY WATER SEALER
ARB-06	N/A	WOOD VARNISH
ARB-07	N/A	ACRYLIC WATER SEALER
ARB-08	N/A	TEST SAMPLE LATEX PAINT #1
ARB-09	N/A	TEST SAMPLE LATEX PAINT #2
ARB-10	N/A	TRAFFIC MARKING PAINT
ARB-11	N/A	TEST SAMPLE LATEX PAINT #4
ARB-12	N/A	TEST SAMPLE LATEX PAINT #3
ARB-13	N/A	WATER-BASED FAST DRYING ACRYLIC (STAIN BLOCKING PRIMER-SEALER ENAMEL UNDERCOATER)
ARB-14	N/A	TRAFFIC MARKING PAINT
ARB-15	N/A	WOOD TONER/STAIN
ARB-16	N/A	ACRYLIC WATER SEALER

ARB NUMBER	DISTRICT NUMBER	SAMPLE DESCRIPTION
ARB-17	N/A	CLEAR HIGH GLOSS LACQUER
ARB-18	SC-1	LACQUER CEDAR PRIMER
ARB-19	SC-2	CLEAR LACQUER SANDING SEALER
ARB-20	SC-3	CLEAR ACRYLIC WATER-BASE GLOSS LACQUER
ARB-21	SC-4	FLUORESCENT WATER COLOR
ARB-22	SC-5	FLAT BLACK LACQUER
ARB-23	SC-6	GREY PRIMER
ARB-24	SC-7	UNSATURATED POLYESTER RESIN
ARB-25	SC-8	WHITE LACQUER UNDERCOAT
ARB-26	SC-9	UNSATURATED POLYESTER RESIN
ARB-27	SC-10	UNSATURATED POLYESTER RESIN
ARB-28	SC-11	SOLID FILM LUBRICANT
ARB-29	SC-12	SOLID FILM LUBRICANT
ARB-30	SC-13	UNAVAILABLE
ARB-31	SC-14	EPOXY VARNISH
ARB-32	SC-15	UNAVAILABLE
ARB-33	SC-16	WINE RED STRIPE
ARB-34	SC-17	DECO MAUVE
ARB-35 A,B,C	SC-18	EPOXY PRIMER, REDUCER, CATALYST
ARB-36	SC-19	WATER-BASE WHITE ACRYLIC LATEX
ARB-37	SC-20	DARK CADET BLUE METALLIC

ARB NUMBER	DISTRICT NUMBER	SAMPLE DESCRIPTION
ARB-38	SC-21	FRENCH VANILLA
ARB-39 A,B	SC-22	SYNTHETIC ENAMEL HARDENER AND URETHANE CLEAR COAT TO BE ADDED TO SC-20 AND SC-21 IN THE RATIO OF 3 PARTS PAINT TO 1 PART HARDENER TO 1 PART CLEAR COAT
ARB-40	SC-23	MODIFIED ACRYLIC/AQUA CLAD (WATER-BASE) CLEAR METAL LACQUER
ARB-41	SC-24	WATER-BASE PRIMER
ARB-42	SC-25	WATER-BASE TOPCOAT
ARB-43	SC-26	WATER-BASE STAIN
ARB-44	SC-27	HIGH-BUILD POLY PRIMER
ARB-45	SC-28	CLEAR POLYESTER TOPCOAT
ARB-46 A,B	SC-29	EPOXY PRIMER COMPONENT A AND B, MIX RATIO 1:1
ARB-47 A,B	SC-30	EPOXY COATING COMPONENT A AND B, MIX RATIO 1:1
ARB-48 A,B	SC-31	EPOXY LIGHT GRAY WITH EPOXY REACTOR, MIX RATIO 4:1
ARB-49 A,B	SC-32	EPOXY RED - EPOXY REACTOR, MIX RATIO 4:1
ARB-50	MTS-375	ALYKD ENAMEL
ARB-51 A,B	MTS-376 A,B	POLYESTER THERMOPLASTIC WITH CATALYST
ARB-52	MTS-377	TEMPORARY PROTECTIVE COATING
ARB-53	MTS-378	WATER-REDUCIBLE ELECTRIC MOTOR VARNISH

ARB NUMBER	DISTRICT NUMBER	SAMPLE DESCRIPTION
ARB-54 A,B	MTS-379 A,B	WATER-REDUCIBLE INORGANIC ZINC MARINE PRIMER (A:B => 1:1)
ARB-55	MTS-380	PAINT STRIPPER
ARB-56 A,B	MTS-381 A,B	HIGH HEAT EPOXY RESIN (A:B => 100G : 24G)
ARB-57	MTS-382	PRIMER SINGLE PART COATING
ARB-58	MTS-383	WALKWAY COMPOUND
ARB-59 A,B	MTS-384 A,B	ABLATIVE COATING (A:B => 4:1 SMALL QUANTITIES ONLY - 180 SEC POT LIFE)
ARB-60 A,B	MTS-385 A,B	LAMINAR TOPCOAT (A:B => 1:1)
ARB-61 A,B	MTS-386 A,B	HIGH-SOLIDS MARINE PRIMER (A:B =>4:1)
ARB-62 A,B	MTS-387 A,B	POLYURETHANE TOPCOAT(A:B => 1:1)
ARB-63 A,B	MTS-388 A,B	WATER-REDUCIBLE EPOXY PRIMER (A:B => 3:1)
ARB-64	MTS-389	TEMPORARY PROTECTIVE COATING (NOTE: THIS SAMPLE WAS SUBMITTED BY SDCAPCD)
ARB-65	MTS-390	POLYURETHANE
ARB-66	MTS-391	POLYURETHANE
ARB-67	MTS-392	POLYESTER RESIN
ARB-68	MTS-393	POLYESTER RESIN

ARB NUMBER	DISTRICT NUMBER	SAMPLE DESCRIPTION
ARB-69 A,B,C A' (A' = GLOSS)	MTS-394 A,B,C	MULTI-COMP COATINGS BASE SEMI-GLOSS = A BASE GLOSS = A CATALYST = B THINNER/REDUCER = C A:B:C => 4:1:1 A':B:C => 5:1:1
ARB-70 A,B	MTS-395 A,B	POLYESTER RESIN (A:B => 50:1)
ARB-71	MTS-396	ASPHALT BASE HIGH SOLIDS COATING
ARB-72	MTS-397	RIPLEY RESIN/ELECTRICAL INSULATING RESIN
ARB-73 A,B	MTS-398 A,B	CONFORMAL POLYURETHANE RESIN (A:B:THINNER => 100:60:60)
ARB-74	MTS-399	PROTECTIVE ELECTRONICS COATING (COATING:THINNER => 60:100)
ARB-75 A,B	MTS-400 A,B	2-COMPONENT URETHANE(A: B:THINNER => (100:33): 20-50)
ARB-76	MTS-401	THINNNER/REDUCER FOR ARB-73 A,B ARB-74, AND ARB-75 A,B
ARB-77	MTS-402	GRAPHIC ART OFFSET PRINTING INK
ARB-78	MTS-403	PRIMER COATING AND CATALYST
ARB-79	MTS-404	SOLVENT BLEND
ARB-80	MTS-405	NO VOC STAIN
ARB-81 A,B,C	MTS-406 A,B,C	POLYAMIDE EPOXY 3 COMPONENT COATING (A:B:C => 1:1:0.25)
ARB-82 A,B,C	MTS-407 A,B,C	ALIPHATIC POLYURETHANE (A:B:C => 3:1:0.5)
ARB-83	MTS-408	HIGH SOLIDS BAKING ENAMEL

20. E. Data and Comments on Interlaboratory Round Robin Study: Volatile Organic Content (VOC) of Waterborne and Solvent-Based Coatings

<u>CONTENTS</u>